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**Appendix 6**

**Ambient levels of peroxyacetyl nitrate in Southern  
California**

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**prepared for**

**California EPA Air Resources Board  
2020 L Street  
Sacramento, CA 95814**

**prepared by**

**Daniel Grosjean (a)**

**DGA, Inc.  
4526 Telephone Road, Suite 205  
Ventura, CA 93003**

**(a) phone (805) 644-0125, fax (805) 644-0142, e-mail [danieldga@aol.com](mailto:danieldga@aol.com)**

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## Abstract

We examine in this report past and current ambient levels of PAN (peroxyacetyl nitrate,  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ ). PAN has no direct sources and forms in-situ in the atmosphere. PAN is a severe eye irritant, a mutagen and a phytotoxin.

Our study is motivated by the decision to phase out MTBE as an oxygenated additive to gasoline in the State of California. MTBE may be replaced by ethanol. The atmospheric reactions of ethanol and of its vehicle exhaust product acetaldehyde lead to PAN. To assess the possible impact of ethanol on future PAN air quality, it is important to review and analyze current information on ambient levels of PAN in California.

We focus on the urban region that is most severely impacted by photochemical smog, i.e., southern California, where PAN has been measured earlier and more frequently than anywhere else in the world. We examine diurnal, seasonal and spatial variations in ambient PAN and compare these variations to those of ozone. We calculate, using data from several studies, the magnitude of PAN loss by thermal decomposition. We analyze long-term trends in highest, 24 hour-averaged and monthly averaged PAN concentrations. We discuss the relative importance of VOC that are precursors to PAN. We also summarize information regarding PPN (peroxypropionyl nitrate,  $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OONO}_2$ ) and PPN / PAN concentration ratios. Since ethanol and acetaldehyde lead to PAN but not to PPN, the PPN / PAN ratio may be a useful indicator of the impact of ethanol on PAN air quality.

This document is a first draft, and several topics discussed here will continue to be studied. Findings and conclusions to date are as follows:

- Diurnal variations of PAN exhibit mid-day maxima. The time of the maximum PAN concentration varies with location and season and frequently coincides with that of ozone. PAN / ozone concentration ratios exhibit substantial diurnal, spatial and seasonal variations. Thus, ozone, which is measured at numerous southern California monitoring locations, is a poor surrogate for PAN: ozone data can be used to predict the time of maximum PAN but not to estimate PAN concentrations and their diurnal, seasonal and spatial variations.
- Spatial variations of PAN have been studied only twice, in 1987 and 1993. The data indicate formation of PAN during eastward (inland) transport under typical summertime conditions. There is also evidence for vertical transport to mountain locations.
- Seasonal variations of PAN are sparsely documented, and this especially so in the last decade (no data since 1987). Results from earlier studies indicate that high levels of PAN are often recorded outside of the traditional smog season, and that coastal and central regions of the South Coast Air Basin may experience higher levels of PAN during the late fall than during the summer months.

- Calculations of the amount of PAN lost by thermal decomposition at four locations during a two-day summer 1993 smog episode have shown that the amount of PAN that decomposed was comparable in magnitude to that present in ambient air. We have carried out similar calculations using data from SCOS97, and the results also indicate significant thermal decomposition of PAN. While additional calculations are being carried out using data sets from SCOS, SCAQS (1987) and other studies, it appears that thermal decomposition of PAN may account for much of the differences between diurnal, spatial and seasonal variations of ambient PAN and those of ambient ozone.
- Data on ambient PAN in southern California are from ca. 25 studies that span some 35 years. The highest concentrations were recorded during early studies (and often outside the smog season), e.g. 60-65 ppb in the late 1960's. Many of the subsequent studies lasted only a few days, weeks or months, thus providing us with no firm basis to assess long-term trends. High levels of PAN (40 ppb or more) have been recorded until ca. 1980, and concentrations of PAN appear to have decreased substantially thereafter. No PAN concentration higher than 10 ppb has been reported since 1991. The most severe summer smog episode of 1993 yielded highest PAN concentrations of 5.5-9.9 ppb (4 locations) and the highest PAN concentrations measured during SCOS 97 were 4.8 ppb in Azusa and 3.0 ppb in Simi Valley.
- Consistent with the downward trend observed for highest PAN concentrations, 24 hour-averaged PAN concentrations have declined from 15-20 ppb in the late 1960's and until 1980 to 5-12 ppb in 1985-90 and 2-5 ppb in 1993. The most recent 24-hour averages (SCOS 1997) were • 2.1 ppb in Azusa (average =  $0.87 \pm 0.34$  ppb, n = 95) and • 1.3 ppb in Simi Valley (average =  $0.60 \pm 0.23$  ppb, n = 118).
- Very few recent studies have lasted long enough to calculate monthly averaged PAN concentrations. The most recent values (SCOS 97) are  $0.98 \pm 0.83$  ppb (August) and  $0.85 \pm 0.68$  ppb (Sept.) in Azusa and  $0.62 \pm 0.43$  ppb (July),  $0.63 \pm 0.47$  ppb (August) and  $0.53 \pm 0.34$  ppb (Sept.) in Simi Valley.
- PAN may form from the many VOC, including ethanol and acetaldehyde, that lead to the acetyl radical. One section of this report stresses the importance of calculating the relative importance of these VOC as precursors to PAN. Ranking of VOC for their contribution to PAN is being investigated by means of computer simulations using recent input data for VOC. Concurrently, we have begun to examine long-term trends in PAN precursors including NO<sub>x</sub> and VOC, including acetaldehyde, that lead to the acetyl radical. The results will be discussed in a subsequent version of this report.
- To assess human exposure to PAN, it is necessary to have some knowledge of indoor levels of PAN and of indoor / outdoor concentration ratios. With the exception of one study, which is discussed in this report, no information is available regarding indoor PAN in California.
- Ambient levels of PPN have been reported in nine studies, i.e., even less information is available for PPN than for PAN. Highest concentrations of PPN were up to 5-6 ppb in earlier studies and ca. 1 ppb or less in recent years. Twentyfour hour-averaged concentrations range from 0.1 to 1.8 ppb. There are no data for monthly averages, seasonal variations, and indoor concentrations.

- Diurnal variations of ambient PPN are closely related to those of PAN, and linear regression parameters are presented for 10 sets of measurements made in 1989-91, 1993 and 1997. Data for the one location studied in 1993 and 1997 yielded identical results. The slopes of the linear regressions of ambient PPN vs. ambient PAN at all locations studied in 1993 and 1997 range from 0.10 to 0.17 (average = 0.15). These values may serve as a baseline when using the PPN / PAN concentration ratio as an indicator of the possible impact of replacing MTBE by ethanol on future PAN air quality in southern California.

## **List of Tables**

Table 1.	Ozone / PAN concentration ratios at the time of maximum ozone.
Table 2.	Ozone / PAN concentration ratios: ratios of monthly-averaged concentrations.
Table 3.	Summary of data from studies involving simultaneous measurements of ambient PAN at two or more locations.
Table 4.	Summary of data from long-term studies of ambient PAN in Riverside.
Table 5.	Highest PAN concentrations in southern California.
Table 6.	Averaged PAN concentrations in southern California.
Table 7.	Example of calculations of the relative contribution of lumped VOC species to PAN formation.
Table 8.	Indoor and outdoor concentrations of PAN and indoor / outdoor concentration ratios.
Table 9.	Ambient concentrations of PPN in southern California.
Table 10.	Summary of PPN / PAN concentration ratios.

## Figure Captions

- Figure 1. Diurnal variations of PAN: (a) PAN (filled symbols) and PPN (open symbols), Los Angeles, Sept. 9, 1993 (Grosjean et al, 1996) (b) Simi Valley, June 26, 1997 and (c) Azusa, Oct. 5, 1997 (Grosjean and Grosjean, 1999).
- Figure 2. Diurnal variations of PAN and other air quality parameters, Riverside, February 16, 1977. Note the steep increase in PAN, O<sub>3</sub>, NO<sub>2</sub>, CO and light scattering with the arrival of the smog front at ca. 17 PST (Pitts and Grosjean, 1979).
- Figure 3. Time series plot of PAN concentrations during SCAQS, Claremont, August 27-Sept. 3, 1987 (Williams and Grosjean, 1990).
- Figure 4. Diurnal scatterplot of PAN vs. time of day during SCOS, Azusa, July 14 - Oct. 16, 1997 (Grosjean and Grosjean, 1999).
- Figure 5. Composite diurnal profile plots of ambient PAN concentrations: Azusa, July 14-Oct. 16, 1997, and Simi Valley, June 12-Oct. 16, 1997 (Grosjean and Grosjean, 1999).
- Figure 6. Six month-averaged composite diurnal profiles for PAN, Riverside, (a) May 1 - Oct. 31, 1975, (b) Nov. 1, 1975 - April 30, 1996 and (c) May 1 - Oct. 31, 1976 (redrawn from Pitts and Grosjean, 1979).
- Figure 7. Diurnal variations of PAN and ozone: (a) composite diurnal profiles for Tanbark Flat, August 3 - Sept. 5, 1990 (Grosjean et al, 1993); (b) and (c) diurnal profiles for Simi Valley, June 26, 1997 and Azusa, Oct. 5, 1997 (Grosjean and Grosjean, 1999); (d) and (e) composite diurnal profiles for Azusa and Simi Valley, summer 1997 (Grosjean and Grosjean, 1999).
- Figure 8. Diurnal variations of the PAN / O<sub>3</sub> concentration ratio: (a) composite profiles for PAN / O<sub>3</sub> and PPN / O<sub>3</sub>, Tanbark Flat, Aug. 3 - Sept. 5, 1990 (Grosjean et al, 1993); (b) composite profiles for PAN / O<sub>3</sub>, Azusa and Simi Valley, summer 1997 (Grosjean and Grosjean, 1999).
- Figure 9. Spatial variations of PAN during the SCAQS August 28, 1987 smog episode: diurnal profiles at coastal (Long Beach), central (Los Angeles) and inland (Claremont) locations (Williams and Grosjean, 1990).
- Figure 10. Composite diurnal profiles for PAN during the summer 1987 phase of SCAQS: coastal (Long Beach), near-downwind (Azusa) and inland (Claremont) locations (Williams and Grosjean, 1990).
- Figure 11. Spatial variations of PAN: diurnal profiles in Azusa, Claremont, Long Beach and Los Angeles during the Sept. 8-9, 1993 smog episode (Grosjean et al, 1996).

- Figure 12. Spatial variations of PAN: composite diurnal profiles for August 28 - Sept. 13, 1993 in Azusa, Claremont, Long Beach and Los Angeles (Grosjean et al, 1996).
- Figure 13. Spatial variations of PAN: computer simulations of 3-D distribution of PAN at 20:00 PST on August 27, 1987 for a vertical cross-section from Santa Monica Bay to the San Bernardino Mountains (Lu and Turco, 1996).
- Figure 14. Seasonal variations of PAN: time series of daily PAN maxima for the 18-month period May 1, 1975 - Oct. 31, 1976 (a) May - Oct. 75, (b) Nov. 75 - April 76 and (c) May - Oct. 76 (Pitts and Grosjean, 1979).
- Figure 15. Seasonal variations of PAN: twenty-four hour-averaged concentrations of PAN and other pollutants during a winter smog episode, Riverside, February 16 - 21, 1977 (Pitts and Grosjean, 1979).
- Figure 16. Seasonal variations of PAN: diurnal profiles for PAN during the late fall phase of SCAQS. Data for December 3, 1987 at five locations (Williams and Grosjean, 1990).
- Figure 17. Seasonal variations of PAN: Composite diurnal profiles for PAN at three locations during the summer (open symbols) and late fall (solid symbols) phases of SCAQS, 1987 (Williams and Grosjean, 1990).
- Figure 18. Scatterplot of the PAN / O<sub>3</sub> and PPN / O<sub>3</sub> concentration ratios vs. temperature, Tanbark Flat (Grosjean et al, 1993a). Concentrations of PAN, PPN and O<sub>3</sub> are 24-hour averages. Scatterplots of PAN max. / O<sub>3</sub> max. and PPN / max. / O<sub>3</sub> max. vs. temperature, not shown, exhibited the same pattern of decreasing ratios vs. increasing temperature.
- Figure 19. Thermal decomposition of PAN: (a) ambient PAN (solid bars) and concentrations of PAN calculated to have been lost by thermal decomposition (cross-hatched bars) in Azusa, Claremont, Long Beach and Los Angeles during the September 8-9, 1993 photochemical episode (Grosjean et al, 1996). (b) data for Claremont are shown in more detail, (c) data for Azusa, August 4, 1997, (d) data for Azusa, Sept. 4, 1997, (e) data for Simi Valley, July 14, 1997, (f) data for Simi Valley, August 4-6, 1997.
- Figure 20. Long-term trends in ambient levels of PAN in southern California. Top: highest PAN concentrations. Bottom: highest 24 hour-averaged concentrations. Drawn from data in Tables 5 and 6.
- Figure 21. Frequency distributions of 24 hour-averaged PAN concentrations, Riverside, May 1975 - October 1976 (Pitts and Grosjean, 1979).
- Figure 22. Computer simulations of PAN production from lumped VOC species at three VOC / NO<sub>x</sub> ratios (Bowman and Seinfeld, 1994).
- Figure 23. Indoor / outdoor concentration ratios for PAN measured at 11 southern California locations (Hisham and Grosjean, 1991a, 1991b).

- Figure 24. Composite diurnal profiles for indoor and outdoor concentrations of PAN, downtown Los Angeles (Olveira Street), July 18-27, 1988 (Hisham and Grosjean, 1991a).
- Figure 25. Frequency distribution of ambient levels of PPN, August 28 - Sept. 13, 1993; data for 4 locations pooled together (Grosjean et al, 1996).
- Figure 26. Spatial variations of PPN: diurnal concentration profiles for Azusa, Claremont, Long Beach and Los Angeles during the Sept. 8-9, 1993 photochemical episode (Grosjean et al, 1996).
- Figure 27. Composite diurnal profiles for PPN and PAN at mountain locations: (a) Tanbark Flat, Aug. 3 - Sept. 5, 1990, (b) Tanbark Flat, August 5-26, 1991, (c) Franklin Canyon, Sept. 4-12, 1991 (Grosjean et al, 1993a).
- Figure 28. Composite diurnal profiles for PPN in Azusa, Claremont, Long Beach and Los Angeles, August 28 - Sept. 13, 1993 (Grosjean et al, 1996).
- Figure 29. Diurnal variations of the PPN / PAN concentration ratio at Tanbark Flat (1989, 1990 and 1991) and Franklin Canyon (1991) (Grosjean et al, 1993a).
- Figure 30. Frequency distribution of the PPN / PAN concentration ratios measured at four southern California locations (data pooled together) from August 28 to Sept. 13, 1993 (Grosjean et al, 1996).
- Figure 31. Examples of scatterplots of ambient PPN vs. ambient PAN: (a) Tanbark Flat, 1990, (b) Tanbark Flat, 1991, (c) downtown Los Angeles and Claremont, 1993, (d) Azusa, 1997, (e) Simi Valley, 1997 (Williams and Grosjean, 1991; Grosjean et al 1993a, 1996; Grosjean and Grosjean, 1999). See linear regression parameters in Table 10.



## 1. Introduction

Peroxyacetyl nitrate (PAN,  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ ) plays an important role in atmospheric chemistry. PAN was first identified in southern California smog as "compound X" and subsequently characterized by Stephens and co-workers in the mid-1950s (Stephens et al, 1956a, 1956b; Scott et al, 1957). PAN has received attention as an eye irritant, a mutagen, a phytotoxin and a possible agent of skin cancer (Darley et al, 1963a; Mudd, 1966; Heuss and Glasson, 1968; Stephens, 1969; Taylor, 1969; Peak and Belser, 1969; Lovelock, 1977; Temple and Taylor, 1983; Kleindienst et al, 1990; Heddle et al, 1993). Early research on PAN has focused on its phytotoxicity (e.g. Darley, 1963a; Stephens, 1969; Taylor, 1969, and references therein). PAN has also received attention as a source of formaldehyde and free radicals, as an interferent in the measurements of ambient  $\text{NO}_2$  by chemiluminescence (a method used in monitoring networks worldwide) and for its role in the long-range transport (regional and global) of reactive nitrogen in the atmosphere (Carter et al, 1981; Singh and Hanst, 1981; Grosjean, 1983; Grosjean and Harrison, 1985; Singh et al, 1985, 1986).

Quantitative measurements of ambient PAN were first made in Riverside some 35 years ago (Taylor, 1969; U. S. DHEW, 1970; Eschenroeder, 1977). Since then, ambient levels of PAN have been measured many times, first in southern California, subsequently at other urban locations in the U.S. and other countries, and more recently at rural and remote locations throughout the world (e.g. Roberts 1990; Altschuller 1993; Grosjean et al, 1996 and references therein). With a few exceptions, measurements of ambient PAN have been of short duration and have been made as part of intensive research campaigns whose objectives have ranged, for example, from the characterization of severe photochemical smog episodes in urban air to aircraft studies of tropospheric levels of PAN in the Arctic and the tropics. Because of the short duration of these studies, little information is available regarding spatial (e.g. within a given urban area, or region) and seasonal (e.g. winter vs. summer) variations of ambient PAN. There is even less information on long-term trends, due in part to the fact that PAN has received little regulatory attention and is not included in federal, state or local air quality monitoring networks, in the United States or elsewhere.

PAN has no known direct sources and is formed in-situ in the atmosphere in photochemical reactions involving oxides of nitrogen and those volatile organic compounds (VOC) that are precursors to the acetyl radical ( $\text{CH}_3\text{CO}$ ). For example, PAN forms from acetaldehyde as follows:



Competing with reaction (3) above is the reaction of  $\text{CH}_3\text{CO}_3$  with NO:



followed by oxidation of the methyl radical to formaldehyde:



PAN also decomposes back to  $\text{CH}_3\text{CO}_3 + \text{NO}_2$ , i.e., the reverse of reaction 3 (followed by reactions 4 and 5 if NO is present). The rate of decomposition of PAN increases rapidly with increasing temperature (Tuazon et al, 1991; Bridier et al, 1991, and references therein). Thus, ambient levels of PAN are a complex function of temperature (the reverse of reaction 3), of the  $\text{NO}_2 / \text{NO}$  ratio (competition between reactions 3 and 4) and of the abundance and reactivity of those VOC that lead to the acetyl radical. As a result, the relationship between ambient PAN and emissions of its precursors, i.e., VOC and  $\text{NO}_x$ , is highly non-linear, and this even more so than the relationship between ozone, VOC and  $\text{NO}_x$ .

In urban areas, where VOC emissions are often dominated by vehicle emissions, ambient levels of PAN and their long-term variations reflect changes in the magnitude, nature and reactivity of vehicle emissions, i.e., they reflect changes in vehicle fuel policies. The State of California has recently decided to phase out MTBE as an oxygenated additive to gasoline. Of the several vehicle fuel scenarios that may result from this decision, one involves the replacement of MTBE by ethanol. Adding ethanol to gasoline is likely to result in emissions of unburned ethanol (exhaust and evaporative) and of ethanol's incomplete combustion product, acetaldehyde (exhaust). Since ethanol is oxidized to acetaldehyde in the atmosphere, and since acetaldehyde is one of the precursors to PAN, see reaction 1, there is regulatory concern about the possible impact of ethanol on future ambient levels of PAN.

As part of a larger study initiated by the State of California EPA Air Resources Board, we examine in this report past and current levels of PAN with focus on the region that is most severely impacted by photochemical smog, i.e., southern California. PAN has been measured earlier and more frequently in southern California than anywhere else in the world. We examine diurnal, seasonal and spatial variations in ambient PAN. We calculate, using data from studies carried out in the past 20 years, the magnitude of PAN loss by thermal decomposition. The thermal decomposition of PAN leads to formaldehyde, which continues to receive regulatory attention as a toxic air contaminant and for its important role in photochemical smog. We review historical data from research studies, and discuss long-term trends in highest, 24-hour averaged and monthly-averaged PAN concentrations. We discuss the relative importance of VOC that are precursors to PAN. We examine long-term trends in ambient concentrations of compounds that are precursors to PAN, i.e., oxides of nitrogen, acetaldehyde, and hydrocarbons that lead to the acetyl radical. We also summarize information on ambient levels of peroxypropionyl nitrate (PPN,  $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OONO}_2$ ) and on past and recent values of the PPN / PAN ambient concentration ratio, on the assumption that, since the oxidations of ethanol and of its exhaust product acetaldehyde lead to PAN but not to PPN, the PPN / PAN ratio may be a useful indicator of the impact of using ethanol as a vehicle fuel additive on future PAN air quality in southern California.

While this draft report constitutes the first attempt to present a detailed descriptive analysis of ambient PAN in southern California, we need to emphasize that, due to time constraints, the analysis presented in this report is somewhat limited. Several of the topics discussed in this report are being studied in more detail, and the corresponding findings and conclusions will be described in the final report issued at the completion of this project.

## **2. Ambient levels of PAN in southern California**

We describe in this section the diurnal variations of ambient PAN, we compare the diurnal variations of PAN to those of ozone, we examine spatial variations of PAN in southern California, we discuss seasonal variations, and we estimate, using data from several studies, how much PAN is lost to thermal decomposition. Data for peroxypropionyl nitrate (PPN), which will be discussed in Section 5, are shown along with data for PAN in several figures.

### **2.1. Diurnal variations**

Diurnal variations of PAN in urban air exhibit mid-day maxima. The time of the maximum varies with location and season, see discussion of spatial and seasonal variations in Sections 2.3 and 2.4, respectively. For downtown Los Angeles, PAN concentrations are typically highest around noon, see examples in Figure 1. For locations further inland, i.e., smog receptor sites, the diurnal variations of PAN often include a sharp, almost "step-function" increase at the time the "smog front" reaches that location, see example in Figure 2.

Most studies of PAN have been made over periods of several days or weeks, and three types of plots are useful for discussion of diurnal variations of PAN. The first type is a time series plot of concentration vs. time for several consecutive days (for example a multiday smog episode). An example of time series plot is given in Figure 3, using SCAQS data for Claremont in August 1987. The second type, called diurnal scatterplot, consists of combining all observations made over several days (weeks, months) in a scatterplot of concentrations vs. time of day. An example of diurnal scatterplot is given in Figure 4 for ambient PAN in Azusa during SCOS 97. The third type, called a composite diurnal profile, is constructed by averaging all values obtained at a given time and plotting the averages vs. time of day. Examples of composite diurnal profiles constructed from data obtained in short-term studies are shown in Figure 5. Composite diurnal profiles are also useful to analyze data from long-term studies. This is shown in Figure 6, which has been constructed from three consecutive periods of 6 months of PAN data for Riverside, May - October, 1975 ("summer"), November 1975 - April 1976 ("winter") and May - October, 1976 (summer). Time series, diurnal scatterplots and composite diurnal profiles that describe diurnal variations of PAN serve different purposes, e.g. composite diurnal profiles are useful to analyze data in terms of human exposure or damage to vegetation.

### **2.2. Comparison of diurnal variations of PAN and ozone**

Many of the ca. 25 studies carried out in southern California over the last thirty five years have involved simultaneous measurements of PAN and ozone. These studies have shown that, irrespective of location and season, the time of PAN maximum and the time of ozone maximum often coincide, as expected since PAN and ozone have a common photochemical origin. This is shown in Figure 7 using data from several studies as examples (numerous other examples have

been given in the literature, see the references cited in Section 3). From this large body of supportive evidence, it is possible to predict the time of maximum PAN at the many locations where PAN is not measured but where ozone is monitored round the clock every day of the year as part of state and local monitoring networks.

While ozone and PAN exhibit daily maxima at the same time, the ratio of their concentrations at that time may vary substantially from day to day and from one location to the next. These ratios are summarized in Table 1 and Table 2. Table 1 includes ozone / PAN concentration ratios at the time of maximum ozone, compiled using data from studies of short duration and for specific days. Table 2 includes O<sub>3</sub> / PAN concentration ratios calculated from monthly averages measured in the long-term studies of Taylor (1969) and Pitts and Grosjean (1979). The data in Table 1 indicate that O<sub>3</sub> / PAN ratios at the time of maximum ozone range from ca. 13 to 22 during the smog season. Ratios measured outside of the smog season are lower, e.g. ca. 5 to 9 in Nov. - Dec. 1987. In the same way, the data in Table 2 indicate that ozone / PAN ratios of monthly averaged concentrations are lower during the winter than during the smog season.

Ozone / PAN concentration ratios vary substantially during the course of the day, see examples in Figure 8. In general, the ozone / PAN ratio is lowest at night and highest during the day. The highest ozone / PAN ratios are observed during the midday period which includes the time of ozone (and PAN) maximum. Thus, ozone data can be used as a surrogate for PAN data to estimate the time of maximum PAN but not to estimate PAN concentrations. There are several possible reasons for the observed diurnal and seasonal variations in the O<sub>3</sub> / PAN concentration ratio (Grosjean et al, 1993). One contributing factor is the thermal decomposition of PAN, i.e., an increasing fraction of the PAN formed photochemically is "lost" when the temperature increases (day > night, also summer > winter and inland areas > coastal areas). The thermal decomposition of PAN is discussed in Section 2.5.

### **2.3. Spatial variations**

PAN, like ozone, forms during transport of air masses that contain VOC and NO<sub>x</sub> emitted in the coastal and central regions and to which more VOC and NO<sub>x</sub> are added during transport. Under typical summertime meteorology, these air masses are transported inland (eastward), and inland locations have historically experienced high levels of ozone and PAN (e.g. Azusa, Glendora, Claremont, Riverside). Eastward transport of PAN with the Los Angeles plume has also been documented at locations further inland, e.g. Palm Springs, where the maximum PAN concentration was recorded at ca. 8-9 p.m. on August 23-25, 1989 (Grosjean and Williams, 1992). In addition to horizontal transport, vertical transport results from increased vertical mixing during the day. As a result, high concentrations of ozone have been measured aloft and at mountain locations, where severe oxidant damage to vegetation has been documented (e.g. Miller and White, 1977; Heck, Mudd and Miller, 1977; Miller et al, 1986; Grosjean and Bytnerowicz, 1993, and references therein).

While much information is available on spatial variations of ozone, much less data are available for PAN, for which all studies carried out prior to 1987 have been limited to one location at any given time. Information on spatial variations of PAN was first obtained in 1987 during SCAQS, which included simultaneous measurements of PAN at nine locations in June - July, seven

locations in August - September, and five locations in November - December (Williams and Grosjean, 1990). The 12-year old SCAQS study remains the most comprehensive study of this type, in southern California or elsewhere. More recently, simultaneous measurements of PAN have been made only twice, and this at four locations during the summer 1993 (Grosjean et al, 1996) and two locations during the summer 1997 (Grosjean and Grosjean, 1999).

Results from the studies carried out in 1987 and in 1993 are summarized in Table 3. They indicate that, when measured on the same summer days, (a) ambient levels of PAN are higher at inland locations than at source-dominated coastal and central locations, and (b) the maximum PAN concentrations are recorded later in the afternoon at inland locations. These two observations are consistent with photochemical formation of PAN during eastward transport. Examples of the data summarized in Table 3 are illustrated in Figures 9-12. Figure 9 shows diurnal profiles of PAN at several locations on August 28, 1987. Figure 10 shows composite diurnal profiles for ambient PAN in Long Beach, Azusa and Claremont during the summer phase of SCAQS. Figure 11 shows PAN concentrations in Long Beach, Los Angeles, Azusa and Claremont during the September 8-9, 1993 smog episode. Figure 12 shows, for the same four locations, the composite diurnal profiles of ambient PAN during the summer 1993 study described by Grosjean, et al (1996).

While the three-dimensional features of ozone concentrations in southern California have long been investigated (e.g. Edinger, 1973), there is little information on vertical transport of PAN and on concentrations of PAN aloft. Lu and Turco (1996) have carried out computer simulations of the three-dimensional patterns for oxidant concentrations during the SCAQS August 27-28, 1987 smog episode. These simulations indicate that high levels of ozone and PAN may be expected aloft, see Figure 13. PAN has been measured at one San Gabriel Mountains location, Tanbark Flat, during three consecutive smog seasons, 1989, 1990 and 1991 (Williams and Grosjean, 1991; Grosjean et al, 1993a; the highest PAN concentration measured was 22 ppb) and at one location in the Santa Monica Mountains (Grosjean et al, 1993a). No data are available for southern California mountain locations since 1991.

## **2.4. Seasonal variations**

Only limited information is available regarding seasonal variations of PAN. This information comes from the early studies, both carried out in Riverside, of Taylor (1969) for the 9-month period August 1967-April 1968 and of Pitts and Grosjean (1979) for the 18-month period May 1975 - October 1976. All other studies carried out in southern California have been of 5 months duration or less. Of these, the longest are the two 1980 studies of Temple and Taylor (1983) in Riverside (5 and 4 months) and the 1997 SCOS study of Grosjean and Grosjean (1999) in Simi Valley (4 months) and Azusa (3 months). While no study of PAN covering a complete calendar year has been made in southern California, the importance of long-term monitoring of PAN has been recognized elsewhere. In the U. S., the longest study is that of Lewis et al (1983), who measured ambient PAN in New Brunswick, NJ, from September 25, 1978 to May 16, 1980 (20 months). In other countries, PAN has been measured for one year in Delft, the Netherlands (Guicherit and Schulting, 1986), for one year in Creteil near Paris, France (Tsalkani et al, 1991), for two years in Montelibretti near Rome, Italy (Ciccioli et al, 1994), for over two years at Harwell, a rural location in southern England (Dollard et al, 1991), and for five years at a non-urban location in Nova Scotia, Canada (Bottenheim et al, 1994).

Results of the studies of Taylor (1969), Pitts and Grosjean (1979) and Temple and Taylor (1983) are summarized in Table 4, which includes, for each month, the highest PAN concentrations recorded and the monthly-averaged PAN concentrations. Overall, the data in Table 4 are not supportive of a simple scenario in which PAN concentrations, like those of ozone, would be substantially higher during the smog season than during the winter months. The monthly averages of Taylor (1969) are highest in October and November, those of Temple and Taylor (1983) are highest in September and October (with the caveat that both studies did not include the months of May, June and July) and those of Pitts and Grosjean (1979) exhibit a broad maximum in June - September 1975 and a maximum in May in 1976. In these studies, some of the highest PAN concentrations ever measured in southern California have been recorded outside of the smog season, e.g. 58 ppb in November 1968 and 38 ppb in March 1969 (Taylor, 1969), 25 ppb in November 1975, 25 ppb in January 1976, 24 ppb in February 1976, 26 ppb in April 1976 and 32 ppb in May 1976 (Pitts and Grosjean, 1979) and 23, 36 and 30 ppb in February, April and November 1980, respectively (Temple and Taylor, 1983). The frequent occurrences of high levels of PAN outside of the smog season are illustrated in Figure 14, which includes plots of daily PAN maxima in Riverside for the three consecutive six-month periods May-October 1975, November 1975 - May 1976, and May-October 1976 (Pitts and Grosjean, 1979). The corresponding six-month averaged composite diurnal profiles are shown in Figure 13. Six-month averaged PAN concentrations were 3.5 ppb in May-October 1975, 3.05 ppb in November 1975 - April 1976, and 4.1 ppb in May-October 1976 (Pitts and Grosjean, 1979), i.e., on the average wintertime levels of PAN were only ca. 15-25% lower than those measured during the smog season.

High levels of PAN have also been measured outside of the "traditional" smog season in short-term studies carried out in southern California and elsewhere. Pitts and Grosjean (1979) have described a February, 1977 smog episode during which PAN reached 27 ppb in Riverside (Figure 15). Singh et al (1981) reported 17 ppb of PAN in April 1979 in Los Angeles, and Singh and Salas (1989) measured 7 ppb of PAN in February 1984 in Downey. During the late fall phase of SCAQS, up to 13-19 ppb PAN were measured at five locations in late November and early December, 1987 (Williams and Grosjean, 1990). Diurnal profiles for PAN at these locations are shown in Figure 16 for December 3, 1987. Composite diurnal profiles for summer (14 days in June-September) and late fall (6 days in November and December) ambient PAN during SCAQS are compared in Figure 17 for Burbank, Long Beach and Los Angeles. They indicate that late fall levels of PAN at coastal and central locations were higher than (Long Beach, Burbank) or as high as (downtown Los Angeles) those measured during the smog season (Williams and Grosjean, 1990). Outside of California, high levels of PAN have also been measured during the late fall and winter months in Creteil near Paris, France (Tsalkani et al, 1987) and in Tokyo, Japan (Kaneyasu et al, 1995).

As discussed by Williams and Grosjean (1990), high levels of PAN outside of the smog season may reflect unfavorable meteorology (lower mixing heights and less transport of VOC and NO<sub>x</sub> than during the summer) together with less (as compared to summer) loss of PAN by thermal decomposition. Thus, thermal decomposition of PAN appears to play an important role in the diurnal, spatial and seasonal variations of ambient PAN as well as in the variations of the PAN / O<sub>3</sub> concentration ratios. The thermal decomposition of PAN is discussed in the next section.

## 2.5. Thermal decomposition of PAN

We have noted in Section 2.2 that the PAN / O<sub>3</sub> concentration ratio exhibits substantial diurnal variations that include nighttime maxima and mid-day minima (see Figure 7). As is shown in Figure 18 using the data from Tanbark Flat as an example, scatterplots of the average PAN / average O<sub>3</sub> and maximum PAN / maximum O<sub>3</sub> concentration ratios vs. temperature indicate that these ratios decrease with increasing temperature. The thermal decomposition of PAN occurs at significant rates at (and above) ambient temperatures. For example, the lifetime of PAN at atmospheric pressure and T = 298K is about 35 minutes (Tuazon et al, 1991).

The kinetics of the thermal decomposition of PAN have been studied many times (e.g. Bridier et al, 1991; Tuazon et al, 1991, and references therein). The reactions of interest are:



with  $k_3 = 2.52 \times 10^{16} e^{-13,573 / T} \text{ s}^{-1}$  and  $k_1 / k_2 = 1.95 \pm 0.28$ , independent of temperature in the range 283-313 K (Tuazon et al, 1991). From reactions (1-3) above, loss of PAN due to thermal decomposition is given by:

$$- d \text{ PAN} / dt = (k_2 k_3 \text{ PAN NO}) / (k_2 \text{ NO} + k_1 \text{ NO}_2) \quad (4)$$

where PAN, NO and NO<sub>2</sub> are concentrations. Rearranging equation (4) with  $k_1 / k_2 = 1.95$ :

$$- d (\ln \text{ PAN}) / dt = k_3 / (1 + (\text{NO}_2 / 1.95 \text{ NO})) \quad (5)$$

Using equation (5) and experimental data for PAN, NO, NO<sub>2</sub> and T, Grosjean et al (1996) have calculated the amount of PAN lost by thermal decomposition in Long Beach, Los Angeles, Azusa and Claremont during the September 8-9, 1993 smog episode. The results are shown in Figure 19, in which measured ambient concentrations of PAN are compared to the concentrations of PAN calculated to have been lost by thermal decomposition. Overall, the amount of PAN lost by thermal decomposition was comparable in magnitude to the measured ambient levels, i.e., a substantial fraction of the PAN formed was lost by decomposition. The results show, as expected, strong diurnal variations in the amount of PAN lost by thermal decomposition, with nighttime minima (lower temperatures) and mid-day maxima (at the time of maximum temperature). In several instances, a secondary maximum was observed in the morning hours, reflecting the increase in NO concentrations associated with vehicle traffic. For the 2-day episode studied, more PAN was lost at the inland locations (Azusa and Claremont) than at the central and coastal locations (Los Angeles and Long Beach). This spatial distribution is probably typical of summertime conditions, i.e., the combination of higher temperatures and lower NO / NO<sub>2</sub> ratios at inland locations. As part of this study, we have calculated the amount of PAN lost by thermal decomposition at two locations, Azusa and Simi Valley, during SCOS 1997. The results are also shown in Figure 19 and are consistent with those obtained in 1993 by Grosjean et al (1996), i.e., they indicate that a large fraction of the PAN formed in VOC-NO<sub>x</sub> reactions may

decompose, especially during warm afternoons. Calculations of PAN thermal decomposition are in progress for additional data sets including those acquired during the summer and late fall 1987 phases of SCAQS, the 18-month 1975-76 study of Pitts and Grosjean (1979) and the 1989-91 studies carried out at Tanbark Flat (Grosjean et al, 1993a).

As noted in the Introduction, the thermal decomposition of PAN leads to formaldehyde and to free radicals, thereby "fueling" additional photochemical oxidation reactions (including ozone formation) during transport of polluted air masses across the South Coast Air Basin. Formaldehyde also receives regulatory attention as a toxic air contaminant.

### **3. Trends in ambient levels of PAN in southern California**

We examine in this section the historical data base for ambient PAN in southern California. Highest and time-averaged concentrations of PAN are compiled, and the corresponding long-term trends are discussed. Long-term trends are also examined for the pollutants that are precursors to PAN, i.e., oxides of nitrogen, acetaldehyde and other VOC that lead to the acetyl radical.

#### **3.1. Highest PAN concentrations**

The highest ambient concentrations of PAN at southern California locations are listed in Table 5. The data in Table 5 are from ca. 25 studies that span some 35 years. To our knowledge, PAN has not been measured in southern California in the last two years, i.e., since the end of SCOS in October 1997. Most of the studies cited in Table 5 lasted only a few months, weeks, or even days. These studies provide us with a very incomplete picture of long-term trends of ambient PAN in southern California (and this even though the longer studies cited in Table 5 included more than 20,000 measurements of ambient PAN). Thus, while the data in Table 5 clearly suggest a downward trend in ambient levels of PAN since about 1980, this downward trend may be fortuitous, i.e., the PAN levels of 50 ppb or more that were measured in the late 1960's may still be recorded today (although this is unlikely from examination of long-term data for ozone) if the more recent studies had been made at the "right" location and the "right" time of the year.

The first peer-reviewed measurements of ambient PAN were made in the 1960's in Riverside and in Los Angeles (Darley et al, 1963b; U. S. DHEW, 1970; Taylor, 1969; Lonneman et al, 1976). These studies yielded the highest PAN concentrations measured in ambient air, e.g. 58 ppb in 1967 in Riverside (Taylor, 1969) and 65 ppb in 1968 in Los Angeles (Lonneman et al, 1976). To put these high PAN concentrations in perspective, the highest ozone concentrations recorded in southern California were ca. 650 ppb in 1967 and ca. 500 ppb in 1968 (SCAQMD, 1997). The data of Taylor (1969) and Lonneman et al (1976) would correspond to ozone / PAN concentration ratios of ca. 10. This ratio is consistent with those listed in Table 1.

Several of the early articles on ambient PAN (Stephens 1969; Taylor 1969; Lonneman et al, 1976) cite an unpublished communication of Mayrsohn and Brooks (1965), who reportedly measured 214 ppb of PAN in Los Angeles County in September-October 1965. Since the highest ozone concentration recorded in 1965 anywhere in southern California was ca. 570 ppb (SCAQMD, 1997), the PAN concentration of Mayrsohn and Brooks would correspond to a low (and perhaps unlikely) ozone / PAN concentration ratio of ca. 2.7. Table 5, which contains only

data from peer-reviewed publications, does not include the early results of Mayrsohn and Brooks (1965). However, the highest ozone concentration measured in southern California was 680 ppb in 1955 in downtown Los Angeles. The severity of the smog problem in southern California has been documented as early as 1943 with the first media reports of a "gas attack" on July 26 (SCAQMD, 1997). Therefore, ambient levels of PAN may well have exceeded 100 ppb many times between the mid 1940's and the late 1960's during which PAN concentrations as high as 58-65 ppb were reported (Taylor, 1969; Lonneman et al, 1976).

With the caveat, as noted above, that only incomplete information is available regarding long-term trends in ambient PAN, the data in Table 5 suggest that the highest ambient levels of PAN did not change much from 1967 to ca. 1980 (see discussion by Temple and Taylor, 1983; also note that ozone maxima in 1980 were still high, e.g. 460 ppb in Claremont on October 2, 1980, together with 42 ppb of PAN, Grosjean 1983). Beginning in ca. 1980, ambient levels of PAN in southern California appear to have declined substantially, see Figure 20. Thus, no PAN concentration higher than 10 ppb has been reported since 1991 even though, for example, the summer 1993 PAN measurements of Grosjean et al (1996) were carried out at four locations during a period that included the most severe photochemical smog episodes for that year.

To put the more recent data for southern California in perspective, we note that much higher levels of PAN have been measured at other urban locations during the late 1980's and 1990's: • 30 ppb in 1997 in Mexico City, Mexico (Gaffney et al, 1997), up to 12 ppb in 1994 in Athens, Greece (Suppan et al, 1998), up to 12 ppb in 1991 in Tokyo, Japan (Kaneyasu et al, 1995), up to 34 ppb in 1985-86 in Creteil, near Paris, France (Tsalkani et al, 1991), and 40 ppb in 1992 in Montelibretti near Rome, Italy (Ciccioli et al, 1993). In addition, examination of ozone and other air quality data for large urban areas for which no PAN data are available suggests that high levels of PAN are most likely present downwind of Sao Paulo, Brazil, Cairo, Egypt and Djakarta, Indonesia. In short, it appears that southern California has long relinquished its title of "PAN capital of the world" and today may not even rank in the "top-twenty" urban areas worldwide.

### **3.2. Averaged PAN concentrations**

Reports from studies of ambient PAN in southern California have often included some measure of average PAN concentrations, i.e., 24 hour averages, monthly averages, or averages for the period studied. These averages are compiled in Table 6. Because of length limitations generally prescribed by peer-reviewed journals, authors have often omitted individual measurements from their articles. As a result, we have calculated several of the averages listed in Table 6 using data from tables and figures in technical reports.

The limited information available makes it difficult to present conclusions regarding long-term trends in 24-hour averaged and monthly-averaged ambient PAN concentrations. With this caveat, the data in Table 6, consistent with the data given in Table 5 for the highest PAN concentrations, appear to indicate a substantial decrease since ca. 1980. Twenty four-hour averaged PAN concentrations as high as 15-20 ppb have been reported in West Covina (1973), Riverside (1975-76) and Claremont (1980). After 1980, lower 24-hour averages have been measured, the highest values being ca. 5-12 ppb in 1985-1990 and ca. 2-5 ppb thereafter. The most recent 24 hour averages, measured in 1997 during SCOS (Grosjean and Grosjean, 1999), were 0.17-2.08 ppb in Azusa (average =  $0.87 \pm 0.34$  ppb,  $n = 95$ ) and 0.15-1.30 ppb in Simi Valley (average =  $0.60 \pm 0.23$  ppb,  $n = 118$ ).

As was the case for the highest PAN concentrations, high 24-hour averages have been frequently measured outside of the smog season. This is illustrated in Figure 21, which shows the frequency distributions of 24-hour averaged PAN concentrations in 1975-76 in Riverside. More recently, 24-hour averages measured in 1987 in Los Angeles, Burbank and Long Beach were higher during the late fall than during the smog season (Williams and Grosjean, 1990). No measurements documenting wintertime levels of PAN have been made since 1987.

Little information is available regarding monthly averages. Most of this information is for only one location, Riverside, from studies made in 1967-68 (Taylor 1969), 1975-76 (Pitts and Grosjean, 1979) and 1980 (Temple and Taylor, 1983). Monthly averages were 1.0 - 8.1 ppb in 1967-68, 1.6 - 6.8 ppb in 1975-76, and 0.4 - 9.4 ppb in 1980. Very few of the more recent studies have been sufficiently long to calculate monthly averages, and there is no recent information regarding monthly averages outside of the smog season. Monthly averages in Tanbark Flat were 2.2 ppb in August 1989, 2.8 ppb in Sept. 1989, and 4.7 ppb in August 1990. There is no information for the years 1991 to 1996. Monthly averages in 1997 during SCOS were 0.5 - 1.0 ppb, i.e.,  $0.98 \pm 0.83$  ppb (August) and  $0.85 \pm 0.68$  ppb (Sept.) in Azusa and  $0.62 \pm 0.43$  ppb (July),  $0.63 \pm 0.47$  ppb (August) and  $0.53 \pm 0.34$  ppb (Sept.) in Simi Valley.

To summarize, examination of data for highest, 24 hour-averaged and monthly averaged PAN concentrations measured in southern California within the past ca. 35 years suggests an apparent decrease in ambient levels of PAN since ca. 1980. Factors that have a direct influence on ambient levels of PAN include temperature, ambient levels of oxides of nitrogen, and ambient levels of several VOC including acetaldehyde. VOC that are important as precursors to PAN are discussed in Section 3.3 below. Trends in concentrations of VOC, of acetaldehyde and of oxides of nitrogen are discussed in Section 3.4.

### **3.3. VOC precursors to PAN and their relative importance**

The amount of PAN that forms in the atmosphere depends on the emission rates of the VOC that lead to the acetyl radical ( $\text{CH}_3\text{CO}$ ). These VOC include ethanol, acetaldehyde, alkanes, alkenes and aromatics. In addition, the carbonyls that form as first-generation products of the atmospheric oxidation of virtually all VOC include a number of aldehydes and ketones whose subsequent reactions lead to the acetyl radical.

The relationship between PAN and its VOC precursors has been discussed by Williams and Grosjean (1991), Altschuller (1993) and Grosjean et al (1993). The VOC that lead to PAN can be divided into two groups, of which one leads to acetaldehyde and the other to dicarbonyls (e.g. methylglyoxal,  $\text{CH}_3\text{COCHO}$ , and biacetyl,  $\text{CH}_3\text{COCOCH}_3$ ). Ethanol, alkenes such as propene, cis-2-butene and trans-2-butene and alkanes such as isopentane lead to acetaldehyde. Aromatic hydrocarbons, including toluene, xylenes and trimethylbenzenes, are the major precursors of dicarbonyls.

The yield of PAN from each VOC precursor, e.g. ppb PAN formed per ppbC reacted toluene (at a given VOC /  $\text{NO}_x$  ratio) could be calculated for each VOC if we had a detailed knowledge of the VOC oxidation mechanism, including the branching ratios for the pathway(s) that lead to the acetyl radical. This mechanistic information is not available for many VOC. Computer chemical

mechanisms describe VOC oxidation using "lumped" species, which are used as surrogates for groups of VOC that have similar structure and reactivity (e.g. Carter, 1990). As an approximation to assessing the contribution of individual VOC to the formation of PAN, one can use computer chemical mechanisms to estimate the contribution of each lumped species to PAN formation. This can be done using several methods, e.g. by "blanking out" the reactions of a given lumped species in the overall mechanism, by setting the initial concentration = zero for the lumped species of interest, by using "tags" for PAN that forms from a given lumped species (e.g. PAN1 from ethanol, PAN2 for one lumped species of alkenes, PAN3 for one lumped species of aromatics, and so on), or by using the "counter species" method, in which dummy species are added to each reaction that yields any product of interest, in this case PAN. These methods are not strictly equivalent but they should give the same qualitative ranking of VOC with respect to PAN formation.

For example, the counter species method has been used to rank VOC precursors to PAN (Bowman and Seinfeld, 1994) in a simple scenario that involved speciated VOC emissions for August 27, 1987, no dilution and no new emissions, and other input data typical of summertime conditions in Los Angeles. The results are illustrated in Figure 22 for three VOC / NO<sub>x</sub> ratios: 4, 8.2 and 20 ppmC / ppm. On a ppb PAN formed / ppbC emitted VOC basis, acetaldehyde dominates PAN formation, followed by (in decreasing order) higher molecular weight aldehydes, olefins and aromatics. This ranking remains the same at lower and higher VOC / NO<sub>x</sub> ratios, but for these ratios much less PAN is produced (little NO<sub>2</sub> is available to form PAN at higher VOC / NO<sub>x</sub>, and fewer acetyl radicals are formed at lower VOC / NO<sub>x</sub>). To calculate the relative contribution of each lumped VOC species to PAN formation, one multiplies the ppb PAN / ppbC VOC yields shown in Figure 22 by the initial concentrations of the lumped VOC species. Since acetaldehyde concentrations are often lower than those of alkenes, alkanes and aromatics, the contribution of acetaldehyde to PAN formation may be less than that of other VOC. This is shown in Table 7 for the specific example chosen by Bowman and Seinfeld (1994), who used the condensed SAPRC 90 mechanism and VOC emissions from SCAQS 1987. In this particular case, PAN production after 10 hours was dominated by alkenes, alkanes and aromatics, and acetaldehyde accounted for only ca. 11 percent of the total PAN produced. This example is shown only for illustrative purposes, see below.

Since 1987, there have been significant changes in vehicle fuel composition, emission factors for mobile sources, and emission profiles for speciated VOC (possibly including acetaldehyde). Emission inventories have also been substantially updated. In addition, the treatment of PAN formation in earlier versions of computer chemical mechanisms varies substantially from one model to the next, leading to widely different calculated PAN concentrations (e.g. Hough, 1988). For example, the calculated contribution of aromatic hydrocarbons to PAN formation in a scenario typical of urban conditions was 25 times higher when using the Carbon Bond-4 mechanism than when using the RADM2 mechanism (Luecken et al, 1999). Thus, it is important to assess the relative contribution of VOC to PAN formation using current data and up-to-date computer chemical mechanisms. To this end, a series of computer simulations has been initiated, as a joint effort involving DGA and ARB staff, to provide baseline information on VOC precursors to PAN as of 1999, i.e., before ethanol replaces MTBE as a vehicle fuel additive. The results of these simulations will be included in the next version of this report.

### **3.4. Long-term trends in ambient levels of PAN precursors: NO<sub>x</sub>,**

## **acetaldehyde, and other VOC**

Working jointly with ARB staff, we have begun to assemble, organize and analyze long-term data for ambient levels of NO<sub>x</sub>, acetaldehyde, and hydrocarbons in southern California. The results of this descriptive analysis of long-term trends in ambient concentrations of PAN precursors will be included in the next version of this report.

## **4. Exposure to PAN**

### **4.1. General considerations**

National and State Ambient Air Quality Standards (AAQS) for criteria pollutants are motivated by concern for protection of human health. A secondary motivation is concern for damage to vegetation. There is no AAQS for PAN, although its adverse effects on human health and its phytotoxicity have been long recognized (see references cited in the Introduction).

To relate human exposure (via inhalation) to ambient levels of PAN, one needs to translate ambient concentrations into units of dose, e.g. micrograms per day. Recognizing that most people spend much more time indoors than outdoors, one also needs information on indoor concentrations of PAN and on indoor / outdoor relationships.

To estimate dose via inhalation is a simple matter of conversion of units. The molecular weight of PAN (CH<sub>3</sub>C(O)OONO<sub>2</sub>) is 121, 1 ppb of PAN is ca. 4.95 µg m<sup>-3</sup> at 25° C and p = 1 atm. and the "average adult" breathes ca. 23 m<sup>3</sup> of air per day (this figure can be adjusted up and down for "at risk" groups such as children or the elderly). The daily dose of PAN for an "average adult" breathing air with a 24-hour averaged PAN concentration of 1 ppb is 114 µg. For example, the "average adult", if staying outdoors or if PAN concentrations indoors are the same as those outdoors, would have inhaled 570µg of PAN on September 10, 1993 in Claremont (24-hour averaged PAN concentration = 5 ppb, Grosjean et al, 1993).

For a more realistic estimate of actual exposure to PAN, it is critical to have some knowledge of indoor / outdoor concentration ratios. There is unfortunately very little information regarding indoor PAN. The only studies of this type, in southern California or elsewhere, are those of Hisham and Grosjean (1991a, 1991b). In these studies, indoor and outdoor concentrations of PAN were measured simultaneously (together with those of ozone, NO<sub>2</sub> and other pollutants) at 10 locations during the 1988 and 1989 smog seasons. The impetus for these studies was to survey air quality in museums, historical buildings and other settings that house culturally important collections.

On first examination, one could argue that, even though major southern California museums receive large numbers of visitors, a museum is not representative of typical indoor exposure. However, the surveys of Hisham and Grosjean (1991a, 1991b) included locations with no heating, ventilation or air conditioning (HVAC), locations with HVAC but without chemical filtration, and locations with HVAC and with chemical filtration. Thus, these surveys covered a

range of outdoor / indoor air exchange situations that brackets those encountered in dwellings where most people spend their time indoors, i.e., homes, offices, schools and shopping malls. While recommendation is made to better characterize indoor levels of PAN, the results of Hisham and Grosjean (1991a, 1991b) are summarized in the following section and may serve as a guide for future work.

#### **4.2. Indoor levels of PAN and indoor / outdoor concentration ratios**

Hisham and Grosjean (1991a, 1991b) carried out indoor and outdoor measurements of PAN at ten locations, with each location being studied for ca. 2 weeks (locations and dates are listed in Table 2). Indoor and outdoor concentrations of PAN and the corresponding indoor / outdoor concentration ratios are summarized in Table 8. Indoor concentrations of PAN ranged from below detection to 14 ppb, and the outdoor concentrations measured simultaneously ranged from 4 to 14 ppb. The indoor / outdoor concentration ratio varied substantially, depending on whether HVAC was available and, when present, whether the HVAC system used also included a chemical filtration system (e.g. activated carbon). Averaged indoor / outdoor concentration ratios are summarized in Figure 23. Of the four locations that were equipped with HVAC and chemical filtration, as may be the case in a few upscale office buildings and shopping centers, only two yielded the expected results, i.e., low indoor / outdoor PAN concentration ratios. At locations equipped with HVAC, as may be the case in homes, office buildings and shopping malls, indoor concentrations of PAN were only ca. 30% lower than outdoor levels. At locations that lacked HVAC, as is the case in many dwellings and schools in southern California, indoor concentrations of PAN were essentially the same as outdoors ones, see example in Figure 24.

#### **4.3. Factors that may affect indoor levels of PAN**

### **5. Peroxypropionyl nitrate (PPN) and the PPN / PAN ratio**

In the preceding sections, we have reviewed ambient levels of PAN in southern California and discussed possible long-term trends. In addition to PAN, two peroxyacyl nitrates ( $\text{RC(O)OONO}_2$ ) have been measured in ambient air in southern California: peroxypropionyl nitrate (PPN,  $\text{R} = \text{CH}_3\text{CH}_2\text{—}$ ) and peroxy-n-butyryl nitrate (PnBN,  $\text{R} = \text{CH}_3\text{CH}_2\text{CH}_2\text{—}$ ). PPN and PnBN are mutagens (Kleindienst et al, 1990), eye irritants, and are several times more phytotoxic than PAN (Taylor, 1969). PPN and PnBN form as products of the oxidation of VOC that lead to the propionyl ( $\text{CH}_3\text{CH}_2\text{C(O)—}$ ) and n-butyryl ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{C(O)—}$ ) radicals, respectively (Williams and Grosjean, 1991, Altschuller, 1993, Grosjean and Williams, 1993a, 1993b). These peroxyacyl nitrates may serve as indicators of the impact of changes in vehicle fuel composition on PAN air quality, see below.

One of the vehicle fuel scenarios that may result from the State of California's decision to phase out MTBE involves the replacement of MTBE by ethanol. The atmospheric oxidation of ethanol (and of its incomplete combustion product acetaldehyde emitted in vehicle exhaust) leads to PAN; that of MTBE does not. In addition, the oxidations of ethanol and acetaldehyde lead to PAN but not to PPN, PnBN or other peroxyacyl nitrates. Thus,  $\text{RC(O)OONO}_2$  / PAN ambient concentration ratios may be used as diagnostic tools when assessing the impact of ethanol on

PAN air quality. For example, the ratio PPN / PAN is expected to decrease if the use of ethanol as a gasoline additive results in higher emissions of ethanol and acetaldehyde, which form PAN but not PPN.

Ambient levels of PnBN have been measured in only one study carried out at one location, Tanbark Flat (Grosjean et al, 1993b), and as a result the PnBN / PAN concentration ratio measured in that study has limited diagnostic value. Thus, we focus in this section on PPN and on the PPN / PAN ratio. We review literature data for ambient concentrations of PPN in southern California, including highest values, 24-hour averages, diurnal profiles and spatial variations. We also summarize available information regarding the PPN / PAN ratio, whose current values may serve as a "baseline" when assessing the possible impact of replacing MTBE by ethanol on future PAN air quality.

### **5.1. Ambient concentrations of PPN**

The first measurement of ambient PPN appears to be the one of Darley et al (1963), who reported ca. 6 ppb of PPN along with ca. 50 ppb of PAN in a sample collected in Riverside on a smoggy afternoon. Only eight other studies of ambient PPN have been carried out in southern California. Singh and co-workers have carried out two brief studies, one in 1979 in Los Angeles (Singh et al, 1981) and the other in 1984 in Downey (Singh and Salas, 1989). Three studies have been carried out in 1989, one involving round-the-clock measurements for two months at a mountain location, Tanbark Flat (Williams and Grosjean, 1991) and the other involving surveys of ca. 2 days each in Perris and Palm Springs (Grosjean and Williams, 1992). PPN was also measured at Tanbark Flat during the 1990 and 1991 smog seasons, and at another mountain location, Franklin Canyon in the Santa Monica Mountains, during the 1991 smog season (Grosjean et al, 1993a). Spatial variations of PPN in the Los Angeles area were first studied in 1993 by measuring PPN simultaneously at four locations (Azusa, Claremont, Long Beach and Los Angeles) during a ca. two-week period that included severe smog episodes (Grosjean et al, 1996). The latest study of ambient PPN in southern California has involved simultaneous measurements of PPN at two locations, Azusa and Simi Valley, on IOP days during SCOS 1997 (Grosjean and Grosjean, 1999).

The results of the studies cited above are summarized in Table 9, which includes highest, study-averaged, and 24-hour averaged PPN concentrations. Highest concentrations of PPN range from up to ca. 5-6 ppb in the earlier studies to ca. 1 ppb or less in recent years. Twenty four-hour averaged concentrations range from ca. 0.1 to 1.8 ppb, with the lower values being those reported in recent years. The relationship between highest and median PPN concentrations is illustrated in Figure 25, which shows a frequency distribution of all data from measurements made at four locations between August 28 and Sept. 13, 1993. The highest PPN concentration was 1.5 ppb (on Sept. 10 in Azusa) and most of the PPN concentrations measured during that period were ca. 0.2-0.4 ppb.

Diurnal and spatial variations of PPN are similar to those of PAN, and only a brief summary of these variations is given here along with examples. Diurnal variations of PPN exhibit mid-day maxima, see Figure 26 (data for 4 locations during the Sept. 8-9, 1993 smog episode). The mid-day maximum nearly always coincide with that of PAN, see Figure 27. The diurnal variation of the PPN / O<sub>3</sub> concentration ratio is identical to that of the PAN / O<sub>3</sub> concentration ratio and

includes a pronounced mid-day minimum, see Figure 7 in Section 2.1. The PPN / O<sub>3</sub> concentration ratio also decreases with increasing temperature, see Figure 18 in Section 2.5, and this as a result of thermal decomposition. Spatial variations, first studied in 1993, are shown in Figure 28 and indicate, as is the case for PAN, photochemical formation of PPN during transport to inland locations.

No data are available regarding seasonal variations of PPN (all studies have been of short duration, 2 days to 2 months, with focus on the smog season). No data are available regarding indoor levels of PPN and indoor / outdoor concentration ratios.

## **5.2. PPN / PAN concentration ratios**

We have noted earlier that the PAN / O<sub>3</sub> and PPN / O<sub>3</sub> concentration ratios exhibit pronounced diurnal variations. In contrast, the PPN / PAN concentration ratio appears to remain fairly constant during the entire day, see Figure 29. Frequency distribution plots of the PPN / PAN concentration ratios, such as that shown in Figure 30 using summer 1993 data for four locations, indicate that most individual values of the PPN / PAN ratio are within a narrow range, i.e., the ratio remains approximately the same from day to day at a given location. As discussed in detail by Grosjean et al (1993a), spatial and temporal variations in PPN / PAN ratios reflect the combined influence of several parameters including emissions and reactivities of the VOC that are precursors to PPN vs. emissions and reactivities of the VOC that are precursors to PAN. These VOC may include, at least at mountain locations such as Tanbark Flat, biogenic compounds such as isoprene which is a precursor to PAN but not to PPN.

To examine the relationship between ambient PPN and ambient PAN in more detail, several authors have constructed scatterplots of ambient PPN vs. ambient PAN. Examples of these scatterplots are given in Figure 31 for Tanbark Flat, 1990, Tanbark Flat, 1991, Los Angeles, 1993, Claremont, 1993, Azusa, 1997 and Simi Valley, 1997. These scatterplots indicate that PPN and PAN are related in a linear fashion. Linear least squares regression analysis of the data yielded near-zero intercepts, correlation coefficients  $R = 0.79 - 0.98$ , and slopes (PPN / PAN, ppb / ppb) ranging from 0.10 to 0.28. The results of these statistical analyses are compiled in Table 10. For the five locations that were included in the two most recent studies, carried out in 1993 and 1997 (Azusa was included twice, with nearly identical PPN / PAN ratios of  $0.166 \pm 0.018$  in 1993 and  $0.174 \pm 0.005$  in 1997), the slopes of the linear regressions of PPN vs. PAN ranged from 0.10 to 0.17 and averaged 0.15. These values may serve as a baseline when assessing the impact of replacing MTBE by ethanol on PAN air quality in southern California.

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**Table 1. Ozone / PAN concentration ratios at the time of maximum ozone**

Year	Location	Dates	<u>Ozone / PAN ratio, ppb / ppb</u>		Reference
			smog season (mid June to late October)	late fall to late spring (November to mid-June)	
1967	Riverside	Nov. 13 (a)		3.4 (b)	Taylor, 1969
		Nov. 15 (a)		4.4 (b)	Taylor, 1969
1968	Riverside	March 27		6.8 (b)	Taylor, 1969
1973	West Covina	Aug. 24, 31 and Sept. 3-21 and 24-28	11.8 (22) (c)		Spicer, 1977a
	Pasadena	July 24	12.5		Hanst et al, 1975
		July 25	13.3		Hanst et al, 1975
			12.4 (d)		Hanst et al, 1975
		Aug. 9	20.4 (e)		Hanst et al, 1975
1975	Riverside	May 12		17.0	Pitts and Grosjean, 1979
		June 11		15.0	Pitts and Grosjean, 1979
		July 25	15.1		Pitts and Grosjean, 1979
		Aug. 30	13.9		Pitts and Grosjean, 1979
		Oct. 1	13.3		Pitts and Grosjean, 1979
		Nov. 3		11.2	Pitts and Grosjean, 1979
1976	Riverside	March 17		8.5	Pitts and Grosjean, 1979
		June 18		8.6	Pitts and Grosjean, 1979
		July 6	13.5		Pitts and Grosjean, 1979
		Aug. 28	17.3		Pitts and Grosjean, 1979
		Oct. 4	12.7		Tuazon et al, 1978
1977	Riverside	Feb. 16-21		8.3 (6) (e)	Pitts and Grosjean, 1979
		Oct. 11	13.4		Tuazon et al, 1980
1978	Riverside	May 12		10.2 (e)	Pitts and Grosjean, 1979
		July 14	18.2 (e)		Pitts and Grosjean, 1979
		July 25	12.7 (e)		Pitts and Grosjean, 1979
	Claremont	Oct. 9-13	12.3		Tuazon et al, 1979
1979	Claremont	Sept. 1	20.8 (e)		Spicer et al, 1982 (f)
		Sept. 2	20.8 (e)		Spicer et al, 1982 (f)
1980	East Los Angeles (Cal. State U. Los Angeles)	June 26	17.0		Hanst et al, 1982

**Table 1. (continued)**

Year	Location	Dates	Ozone / PAN ratio, ppb / ppb		Reference
			smog season	late fall to late spring	
1980 (cont)	Claremont	Sept. 19 - Oct. 8	13.3 (11)		Grosjean, 1993
1986	Glendora	Aug. 12 - 20	10.0 (9)		Grosjean, 1988a
1987	Anaheim	Nov. 11 - Dec. 11		6.0 (6)	Williams and Grosjean, 1990
	Azusa	June 19 - Sept. 3	21.0 (11)		Williams and Grosjean, 1990
	Burbank	June 19 - Sept. 3	21.0 (11)		Williams and Grosjean, 1990
		Nov. 11 - Dec. 11		4.6 (6)	Williams and Grosjean, 1990
	Claremont	June 19 - Sept. 3	20.0 (11)		Williams and Grosjean, 1990
	Hawthorne	Nov. 11 - Dec. 11		8.9 (6)	Williams and Grosjean, 1990
	Long Beach	June 19 - Sept. 3	16.0 (11)		Williams and Grosjean, 1990
		Nov. 11 - Dec. 11		9.4 (6)	Williams and Grosjean, 1990
	Los Angeles	June 19 - Sept. 3	16.0 (11)		Williams and Grosjean, 1990
		Nov. 11 - Dec. 11		6.5 (6)	Williams and Grosjean, 1990
	Rubidoux	June 19 - Sept. 3	22.0 (11)		Williams and Grosjean, 1990
1989	Tanbark Flat	Aug. 8 - Oct. 16	19.1 (59)		Williams and Grosjean, 1991
1990	Tanbark Flat	Aug. 3 - Sept. 5	14.7 (34)		Grosjean et al, 1993a
1991	Tanbark Flat	Aug. 5-26	19.2 (18)		Grosjean et al, 1993a
1997	Azusa, Simi Valley	July 14 - Oct. 16	36 (95) (g)		Grosjean and Grosjean, 1999
		June 18 - Oct. 16	70 (121) (g)		Grosjean and Grosjean, 1999
			66 (121) (d, g)		Grosjean and Grosjean, 1999

(a) part of an 18-day PAN episode (Taylor, 1969).

(b) calculated using author's data for PAN and for "total oxidants"

(c) average of ratios for the number of days given in parentheses.

(d) at the time of maximum PAN.

(e) estimated from author's data reported as a figure.

(f) PAN data are from Tuazon and co-workers (Spicer et al, 1982).

(g) from composite diurnal profiles of ozone and PAN for entire study.

**Table 2. Ozone PAN concentration ratio: ratios of monthly-averaged concentrations**

Year	Location	Month	Ozone / PAN concentration ratio, ppb / ppb (a)
1967	Riverside (b)	August	14.1
		September	10.6
		October	6.9
		November	5.8
		December	4.0
1968	Riverside (b)	February	27.1
		March	11.4
		April	15.8
1975	Riverside (c)	May	19.7
		June	16.7
		July	18.7
		August	17.0
		September	12.1
		October	13.2
		November	8.5
		December	10.6
1976	Riverside (c)	January	7.3
		February	5.4
		March	8.3
		April	11.0
		May	7.4
		June	10.2
		July	11.6
		August	14.9
		September	14.1
		October	11.0

(a) ratio of monthly average ozone to monthly average PAN.

(b) Taylor, 1969. The ratio is calculated from reported data for PAN and "total oxidants".

(c) Pitts and Grosjean, 1979.

**Table 3. Summary of data from studies involving simultaneous measurements of ambient PAN at two or more locations**

Year	Location	Highest PAN, ppb		Time of PAN max, PST (a)	
		summer	late fall	summer	late fall
1987 (b)	San Nicolas Island	1			
	Long Beach	16	15	13	15
	Hawthorne	< 4-9	16	13-14	15-16
	Anaheim	7	19	13-14	15-16
	Los Angeles	11	13	12	15-16
	Burbank	13	19	14	15-17
	Azusa	13		14	
	Claremont	30		16	
	Rubidoux	14		16-18	
1993 (c)	Long Beach	5.5		12	
	Los Angeles	6.9		12	
	Azusa	6.1		14	
	Claremont	9.9		15-16	
1997 (d)	Azusa	4.8		13	
	Simi Valley	3.0		12	

(a) from composite diurnal profiles reported by the authors.

(b) Williams and Grosjean, 1990.

(c) Grosjean et al, 1996.

(d) Grosjean and Grosjean, 1999.

**Table 4. Summary of data from long-term studies of ambient PAN in Riverside**

Month	Taylor, 1969				Pitts and Grosjean, 1979				Temple and Taylor, 1983 (a)	
	1968		1969		1975		1976		1980	
	Average	Max	Average	Max	Average	Max	Average	Max	Average	Max
January			0.8	8			2.3	25	0.4	8
February			1.4	25			3.9	24	1.3	23
March			3.4	38			3.3	21	2.1	18
April			3.1	21			3.4	26	5.5	36
May					2.8	14	6.8	32		
June					3.5	17	4.8	29		
July					3.8	18	4.9	23		
August	5.9	28			3.6	20	3.0	20	5.6	22
September	5.1	34			4.4	24	2.5	14	9.4	40
October	7.0	43			3.1	24	2.9	19	8.8	42
November	6.9	58			3.7	25			4.2	30
December	0.9	12			1.6	13			1.6	12

(a) daytime measurements, 8 a.m. to 8 p.m., i.e., nighttime maxima may have been missed and monthly averages are not directly comparable to those of the other two studies.

**Table 5. Highest PAN concentrations in southern California**

Year	Location	Study period	Range of daily PAN maxima, ppb	Reference (a)
1962?	Riverside	date not reported	50 (1 sample)	Darley et al, 1963b
1967	Riverside	August 1 - December 31	12-58	Taylor, 1969
1968	Los Angeles	several days, Sept. to Nov.	65	Lonnemann et al, 1976
	Riverside	January 1 - April 30	3-38	Taylor, 1969
1969	—			
1970	—			
1971	—			
1972	—			
1973	Pasadena	several days in July and August	53	Hanst et al, 1975
	West Covina	August 24 - September 28	46	Spicer, 1977a
1974	—			
1975	Riverside	May 1 - December 31	13-25	Pitts and Grosjean, 1979
1976	Riverside	January 1 - October 31	14-32	Pitts and Grosjean, 1979
	Riverside	October 4 - 6	18	Tuazon et al, 1978
1977	Riverside	February 16-21	11-27	Pitts and Grosjean, 1979
	Riverside	July 21, 25, August 10-12 and October 3, 4, 11, 14, 17	18	Tuazon et al, 1980
1978	Claremont	October 9-13	37	Tuazon et al, 1981
	Riverside	Several days, May to July	42	Pitts and Grosjean, 1979
1979	Claremont	August 27 - September 3	10	Spicer et al, 1982 (b)
	Los Angeles	April 9 - 21	17	Singh et al, 1981
1980	Riverside	Jan. 1 - Apr. 30 & Aug. 1 - Dec. 31	8-42	Temple and Taylor, 1983
	East Los Angeles (California State U., Los Angeles campus)	June 26 - 27	16	Hanst et al, 1982
	Claremont	September 19 - October 8	3.5-47	Grosjean, 1983
1981	—			

Table 5 (continued)

Year	Location	Study period	Range of daily PAN maxima, ppb	Reference
1982	—			
1983	—			
1984	Downey	February 18-27	7	Singh and Salas, 1989
1985	Claremont	September 11 - 19	20	Holdren et al, 1986 (c)
1986	Glendora	August 12 - 20	34	Grosjean et al, 1988a
1987	several locations listed below (SCAQS)	Summer : June 19, 24, 25 July 13-15, August 27-31 and Sept. 1-3 Fall: Nov 11-13 and Dec 3, 10, 11		
	Anaheim	Summer Fall	7 19	Williams and Grosjean, 1990 Williams and Grosjean, 1990
	Azusa	Summer	13	Williams and Grosjean, 1990
	Burbank	Summer Fall	13 19	Williams and Grosjean, 1990 Williams and Grosjean, 1990
	Claremont	Summer	30	Williams and Grosjean, 1990
	Hawthorne	Summer Fall	< 4-9 16	Williams and Grosjean, 1990 Williams and Grosjean, 1990
	Long Beach	Summer Fall	16 15	Williams and Grosjean, 1990 Williams and Grosjean, 1990
	Los Angeles	Summer Fall	11 13	Williams and Grosjean, 1990 Williams and Grosjean, 1990
	Rubidoux	Summer	14	Williams and Grosjean, 1990
	San Nicolas Island	Summer	1	Williams and Grosjean, 1990
1988	Los Angeles, downtown (Oliveira Street)	July 18-27	14	Hisham and Grosjean, 1991a
	Los Angeles, downtown (Exposition Park)	August 22 - September 2	5	Hisham and Grosjean, 1991a
	Los Angeles, west (Westwood, UCLA campus)	September 7-16	9	Hisham and Grosjean, 1991a
	Los Angeles, west (Wilshire, George C. Page Museum)	August 29 - September 7	10	Hisham and Grosjean, 1991a

Table 5 (continued)

Year	Location	Study period	Range of daily PAN maxima, ppb	Reference
1988 (cont)	Los Angeles, west (Wilshire, L. A. County Museum of Art)	August 1-15	9	Hisham and Grosjean, 1991a
	Los Angeles, north (Southwest Museum)	September 16 - October 12	10	Hisham and Grosjean, 1991a
	San Marino	August 9-22	12	Hisham and Grosjean, 1991a
	Malibu (J. Paul Getty Museum)	September 12-19	7	Hisham and Grosjean, 1991a
	Ventura	July 26 - August 5	4	Hisham and Grosjean, 1991a
1989	Los Angeles, north (Griffith Park)	August 7-20	8	Hisham and Grosjean, 1991b
	Perris	August 25-27	7	Grosjean and Williams, 1992
	Palm Springs	August 23-25	3	Grosjean and Williams, 1992
	Tanbark Flat (San Gabriel Mountains)	August 8 - October 16	1.5-16	Williams and Grosjean, 1991
1990	Tanbark Flat	August 3 - September 5	3.9-22	Grosjean et al, 1993a
	Tanbark Flat	August 5-26	2.3-12.8	Grosjean et al, 1993a
	Franklin Canyon (Santa Monica Mountains)	September 4-12	2.0-7.0	Grosjean et al, 1993a
1992	—			
1993	Azusa	August 28 - September 13	1.9-6.1	Grosjean et al, 1996
	Claremont	September 1-11	2.4-9.9	Grosjean et al, 1996
	Claremont	September 1-25	4.2	Mackay, 1994
	Long Beach	August 29 - September 13	0.2-5.5	Grosjean et al, 1996
	Los Angeles	August 30 - September 11	0.2-6.9	Grosjean et al, 1996
1994	—			
1995	—			
1996	—			

**Table 5 (continued)**

Year	Location	Study period	Range of daily PAN maxima, ppb	Reference
1997	Azusa	July 14 - October 16	-4.8	Grosjean and Grosjean, 1999
	Simi Valley	June 12 - October 16	-3.0	Grosjean and Grosjean, 1999
1998	—			

(a) PAN was measured using the following methods: Fourier-transform infrared spectroscopy (Hanst et al, 1975, 1992; Tuazon et al, 1978, 1980, 1981; Spicer et al, 1982), coulometry (Singh et al, 1981; results deemed tentative by the authors), luminol (Mackay, 1994) and electron capture gas chromatography, EC-GC (all other studies).

(b) FT-IR PAN data of Tuazon and co-workers (Spicer et al, 1982).

(c) cited in Grosjean, 1988b.

**Table 6. Averaged PAN concentrations in southern California**

Year	Location	Date	Range of monthly averages, ppb	Study average, ppb	Range of 24-hour averages, ppb	Reference
1967	Riverside	August 1 - December 31	1.2 - 8.1	5.2 (a)		Taylor, 1969
1968	Riverside	January 1 - April 30	1.0 - 4.0	2.2 (a)		Taylor, 1969
1973	West Covina	Aug. 24, 31, Sept. 3-14 and Sept. 17-28		9.41	1-20	Spicer, 1977a
1975	Riverside	May 1 - December 31	1.6 - 4.4	3.3 (a)	1-15	Pitts and Grosjean, 1979
1976	Riverside	January 1 - October 31	2.3 - 6.8	3.8 (a)	1-16	Pitts and Grosjean, 1979
1977	Riverside	February 16-21		9 (b)	6-14 (b)	Pitts and Grosjean, 1979
1979	Los Angeles	April 9-12		5.0 ± 4.5		Singh et al, 1981
1980	Claremont	Sept. 19 - Oct. 8			1-20 (b)	Grosjean, 1983
	Riverside	January 1 - April 30	0.4 - 5.5 (c)	2.3 (a, c)		Temple and Taylor, 1983
	Riverside	August 1 - December 31	1.6 - 9.4 (c)	5.9 (a, c)		Temple and Taylor, 1983
1985	Claremont	September 14 - 18			0.3 - 6.9	Grosjean, 1988b
1986	Glendora	August 12-21		13.7		Grosjean, 1988a
1987 (SCAQMS)	Long Beach	summer			0.8-2.9	Williams and Grosjean, 1990
		late fall			1.0-5.0	Williams and Grosjean, 1990
	Los Angeles	summer			1.3-3.7	Williams and Grosjean, 1990
		late fall			0.9-5.2	Williams and Grosjean, 1990
	Anaheim	late fall			1.0-9.0	Williams and Grosjean, 1990
	Burbank	summer			1.0-4.6	Williams and Grosjean, 1990
		late fall			1.3-7.1	Williams and Grosjean, 1990
	Azusa	summer			1.7-4.8	Williams and Grosjean, 1990
	Claremont	summer			2.7-11.6	Williams and Grosjean, 1990

**Table 6 (continued)**

Year	Location	Date	Range of monthly averages, ppb	Study average, ppb	Range of 24-hour averages, ppb	Reference
1988	Los Angeles (d)	July 18 - Oct. 12			0.2-3.1	Hisham and Grosjean, 1991a
	San Marino	August 9-22			1.6-3.2	Hisham and Grosjean, 1991a
	Malibu	September 12-19			0.5-2.9	Hisham and Grosjean, 1991a
	Ventura	July 26 - August 5			0.4-1.4	Hisham and Grosjean, 1991a
1989	Griffith Park	August 7-20			0.3-2.6	Hisham and Grosjean, 1991b
	Tanbark Flat	Aug. 8 - Oct. 16	2.2 (Aug. 8-31) 2.8 (Sept. 1-30)	2.9 (e)	0.9 - 8.2	Williams and Grosjean, 1991
1990	Tanbark Flat	Aug. 3 - Sept. 5	4.7 (Aug. 3-31)	4.8 (e)	2.1 - 10.3	Grosjean et al, 1993a
1991	Tanbark Flat	August 5-26		3.0 (e)	1.0 - 5.1	Grosjean et al, 1993a
	Franklin Canyon	September 4-12		1.6 (e)	1.1 - 2.6	Grosjean et al, 1993a
1993	Azusa	Aug. 28 - Sept. 13		1.8 ± 1.3	0.53-2.96	Grosjean et al, 1996
	Claremont	September 1-11		3.0 ± 1.6	0.81-4.96	Grosjean et al, 1996
	Long Beach	Aug. 29 - Sept. 13		0.9 ± 0.9	0.15-1.94	Grosjean et al, 1996
	Los Angeles	Aug. 30 - Sept. 11		1.1 ± 1.3	0.14-1.61	Grosjean et al, 1996
1997	Azusa	July 14 - October 16	0.98 ± 0.83 (Aug.) 0.85 ± 0.68 (Sept.)	0.88 ± 0.74 (av = 0.87 ± 0.34, n = 95)	0.17 - 2.08	Grosjean and Grosjean, 1999
	Simi Valley	June 18 - October 16	0.62 ± 0.43 (July) 0.63 ± 0.47 (Aug.) 0.53 ± 0.34 (Sept.)	0.61 ± 0.43 (av = 0.60 ± 0.23, n = 118)	0.15 - 1.30	Grosjean and Grosjean, 1999

(a) average of monthly averages listed in Table 4.

(b) estimated from data reported by authors as figures.

(c) from measurements taken from 8 a.m. to 8 p.m.

(d) combining data from the 6 locations listed in Table 5.

(e) average of 24-hour averaged values.

**Table 7. Example of calculation of the relative contribution of lumped VOC species to PAN formation (a)**

Compound or lumped species (b)		Initial concentration, ppbC (c)	Contribution to PAN (d), percent
CO	carbon monoxide	1500	—
CH <sub>4</sub>	methane	1700	—
HCHO	formaldehyde	8	—
CCHO	acetaldehyde	5	2.6
RCHO	higher MW aldehydes (propanal)	2	0.5
MEK	higher MW ketones (2-butanone)	16	1.4
ALK1	low MW, less reactive alkanes	353	18.6
ALK2	higher MW, more reactive alkanes	236	13.5
ARO1	benzene + toluene	147	9.4
ARO2	higher MW aromatics (mostly xylenes)	108	15.2
ETHE	ethylene	75	6.8
OLE1	low MW, less reactive alkenes	60	14.9
OLE2	low MW, more reactive alkenes	29	8.9
OLE3	biogenic compounds (isoprene + terpenes)	62	8.3

(a) adapted from Tables 1 and 5 in Bowman and Seinfeld (1994).

(b) in the condensed version of the SAPRC 90 chemical mechanism.

(c) using SCAQS 87 emission inventory as input data.

(d) at VOC / NO<sub>x</sub> = 8.2 ppbC / ppb.

**Table 8. Indoor and outdoor concentrations of PAN and indoor / outdoor concentration ratios**

Location (a)	indoor PAN, ppb		outdoor PAN, ppb		indoor / outdoor concentration ratio (average of ratios for all paired measurements)
	highest	range of 24-hour averages	highest	range of 24-hour averages	
Los Angeles, downtown (Olveira Street)	14	0.5 - 3.8	14	0.9 - 3.6	1.00 ± 0.10 (no HVAC)
Los Angeles, downtown (Exposition Park)	5	0.4 - 1.0	5	0.3 - 0.7	1.00 ± 0.15 (no HVAC)
Los Angeles, west (Wilshire at La Cienega)	6	0.8 - 2.0	9	1.2 - 3.1	0.67 ± 0.10 (HVAC + CF)
Los Angeles, west (Wilshire at La Brea)	5	0.2 - 1.8	10	1.3 - 2.9	0.65 ± 0.10 (HVAC)
Los Angeles, Westwood	3	BD (b) - 1.0	5	0.2 - 1.4	0.83 ± 0.20 (HVAC)
Los Angeles, northwest (Griffith Park)	0.7	BD - 0.2	8.4	0.3 - 2.6	0.04 ± 0.07 (HVAC + CF) 0.19 ± 0.05 (c)
Los Angeles, north (Southwest Museum)	7	0.3 - 1.6	10	0.7 - 2.6	0.59 ± 0.10 (no HVAC)
San Marino	2	BD - 0.3	12	1.6 - 3.2	0.08 ± 0.05 (HVAC + CF)
Malibu	5	0.5 - 1.7	7	0.5 - 1.9	0.69 ± 0.10 (HVAC + CF)
Ventura	2	0.2 - 0.5	4	0.4 - 1.4	0.55 ± 0.25 (no HVAC)

(a) Adapted from Hisham and Grosjean, (1991a, 1991b). Studies carried out during the summer 1989 (Los Angeles, northwest, Griffith Park) and the summer 1988 (all other locations), see dates in Table 2. HVAC = heating, ventilation and air conditioning system; CF = chemical filtration.

(b) BD = below detection.

(c) measured in a "buffer zone" intermittently open to outdoor air.

**Table 9. Ambient concentrations of PPN in southern California**

Year	Location and dates	PPN, ppb (a)			Reference
		range of daily maxima	study average	range of 24-hour averages	
1962 ?	Riverside (date not reported)		ca. 6 (b)		Darley et al, 1963b
1979	Los Angeles April 9-21	up to 2.7	0.72 ± 0.67		Singh et al, 1981 (c, d)
1984	Downey February 18-27	up to 0.4	0.060 ± 0.067		Singh and Salas, 1989 (d)
1989	Tanbark Flat August 8 - October 16	0.4 - 5.1	0.75	0.09 - 1.8	Williams and Grosjean, 1991
	Palm Springs August 23 - 25	0.42			Grosjean and Williams, 1992
	Perris August 25 - 27	0.73			Grosjean and Williams, 1992
1990	Tanbark Flat August 3 - September 5	0.5 - 4.3	0.69 (e)	0.25 - 1.7	Grosjean et al, 1993a
1991	Tanbark Flat August 5 - 26	0.3 - 2.7	0.43 (e)	0.1 - 0.83	Grosjean et al, 1993a
	Franklin Canyon September 4 -12	0.3 - 1.2	0.18 (e)	0.09 - 0.37	Grosjean et al, 1993a
1993	Azusa August 28 - September 11	0.26 - 1.46	0.47 ± 0.24	0.19 - 0.88	Grosjean et al, 1996
	Claremont September 1 - 11	0.17 - 1.20	0.31 ± 0.17	0.17 - 0.69	Grosjean et al, 1996
	Long Beach August 29 - September 13	0.20 - 0.86	0.25 ± 0.15	0.14 - 0.42	Grosjean et al, 1996
	Los Angeles August 30 - September 11	0.33 - 1.04	0.24 ± 0.18	0.07 - 0.32	Grosjean et al, 1996
1997	Azusa 17 days in July - October (f)	up to 0.72	0.25 ± 0.12		Grosjean and Grosjean, 1999
	Simi Valley 17 days in July - October (f)	up to 0.28	0.13 ± 0.07		Grosjean and Grosjean, 1999

(a) measured by electron capture gas chromatography except in one study (see footnote).

(b) one sample collected during a smoggy afternoon.

(c) measured by coulometry, results deemed tentative by the authors.

(d) instrument not calibrated for PPN, concentrations of PPN reported assuming the same response factor as for PAN.

(e) mean of 24-hour averaged values.

(f) July 17, Aug. 4-6, 21-23 and 26-28, Sept. 4-6, 28 and 29, and Oct. 3 and 4.

**Table 10. Summary of PPN / PAN concentration ratios**

Year	Location and dates	PPN/PAN, ppb/ppb		Intercept, ppt (a)	n	R	Reference
		Ratio	Slope				
1962?	Riverside date not reported	0.12 (b)					Darley et al, 1963b
1979	Los Angeles April 9-21	0.145 (c) 0.163 (d)					Singh et al, 1981 (e)
1984	Downey February 18 - 27	0.05 (c) 0.06 (d)					Singh and Salas, 1989 (e)
1989	Tanbark Flat August 8 - October 16		$0.280 \pm 0.001$	$- 73 \pm 2$	3,000	0.943	Williams and Grosjean, 1991
	Perris August 25 - 27	0.135-0.182 (f)		—	—	—	Grosjean and Williams, 1992
	Palm Springs August 23 - 25	0.127-0.135 (f)		—	—	—	Grosjean and Williams, 1992
1990	Tanbark Flat August 3 - September 5		$0.182 \pm 0.001$	$- 115 \pm 7$	1,400	0.966	Grosjean et al, 1993a
1991	Tanbark Flat August 5 - 26		$0.187 \pm 0.001$	$- 128 \pm 5$	900	0.979	Grosjean et al, 1993a
	Franklin Canyon September 4 -12		$0.140 \pm 0.002$	$- 46 \pm 4$	338	0.964	Grosjean et al, 1993a
1993	Azusa August 28 - September 11		$0.166 \pm 0.018$	$- 24 \pm 23$	331	0.786	Grosjean et al, 1996
	Claremont September 1 - 11		$0.097 \pm 0.014$	$- 4 \pm 7$	403	0.925	Grosjean et al, 1996

**Table 10 (continued)**

Year	Location and dates	PPN/PAN, ppb/ppb		Intercept, ppt (a)	n	R	Reference
		Ratio	Slope				
1993 (cont.)	Long Beach August 29 - September 13		$0.153 \pm 0.030$	$92 \pm 8$	354	0.793	Grosjean et al, 1996
	Los Angeles August 30 - September 11		$0.136 \pm 0.026$	$48 \pm 7$	319	0.897	Grosjean et al, 1996
1997	Azusa several days in July - October (g)		$0.174 \pm 0.005$	$-51 \pm 10$	132	0.943	Grosjean and Grosjean, 1999
	Simi Valley several days in July - October (g)		$0.154 \pm 0.005$	$-15 \pm 6$	138	0.924	Grosjean and Grosjean, 1999

(a) 1 ppt = 0.001 ppb.

(b) PPN / PAN ratio (one sample).

(c) average PPN / average PAN.

(d) highest PPN / highest PAN.

(e) see footnotes (c) and (d) in Table 9.

(f) range of ratios at the time of maximum PPN concentration.

(g) days are listed in footnote (f) in Table 9.

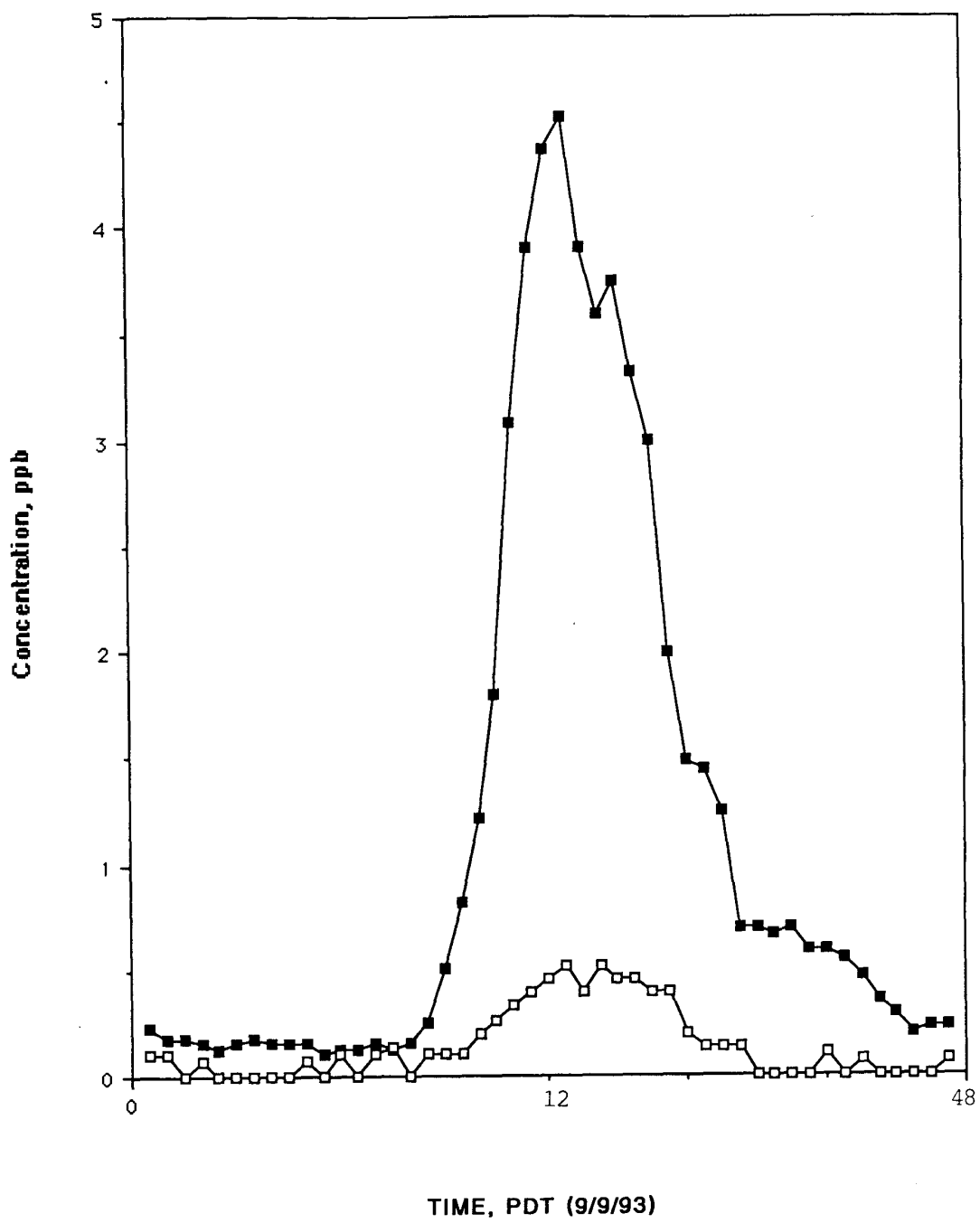


FIGURE 1(a)

Simi Valley 6/26/97

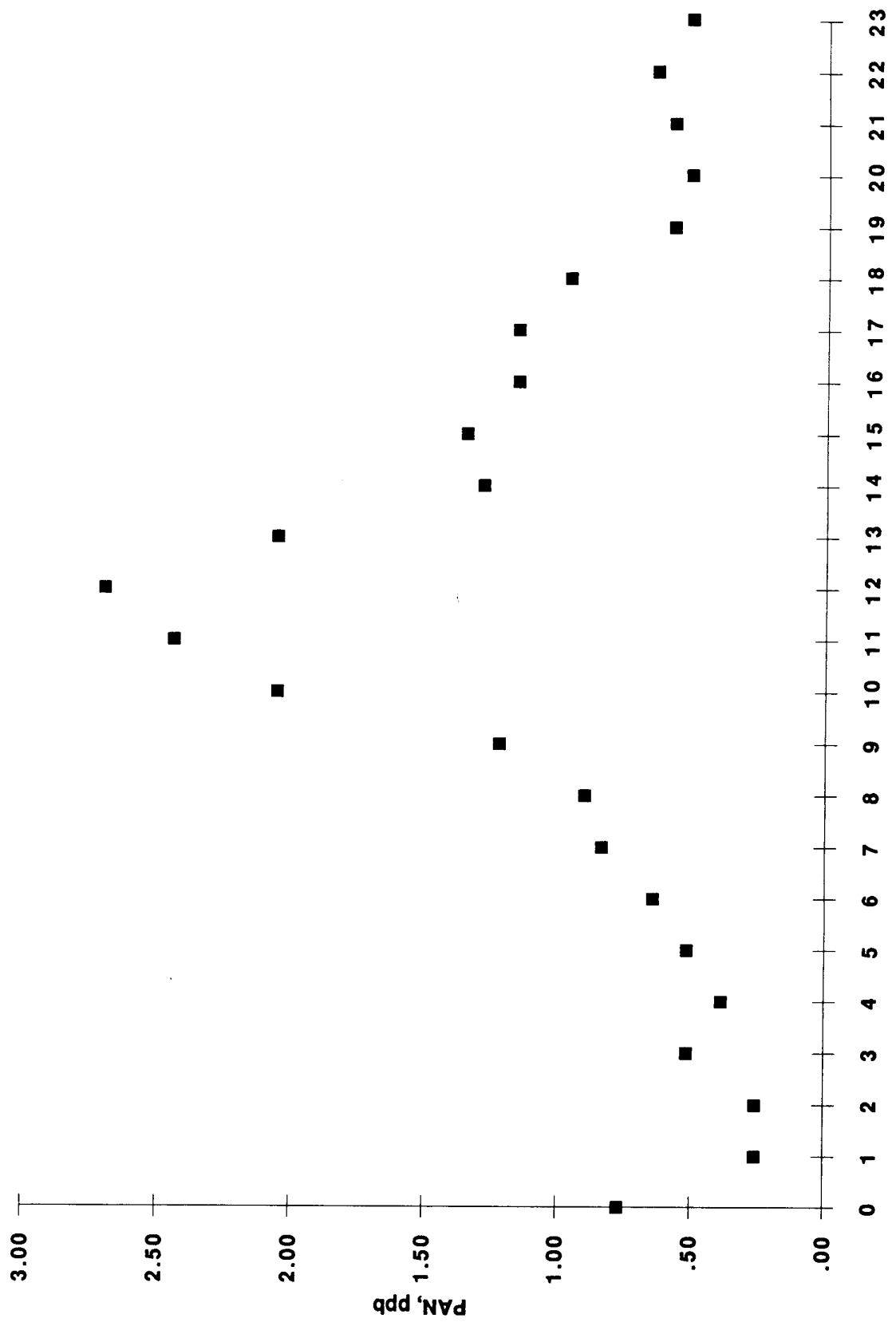


FIGURE 1(b)

Azusa 10/5/97

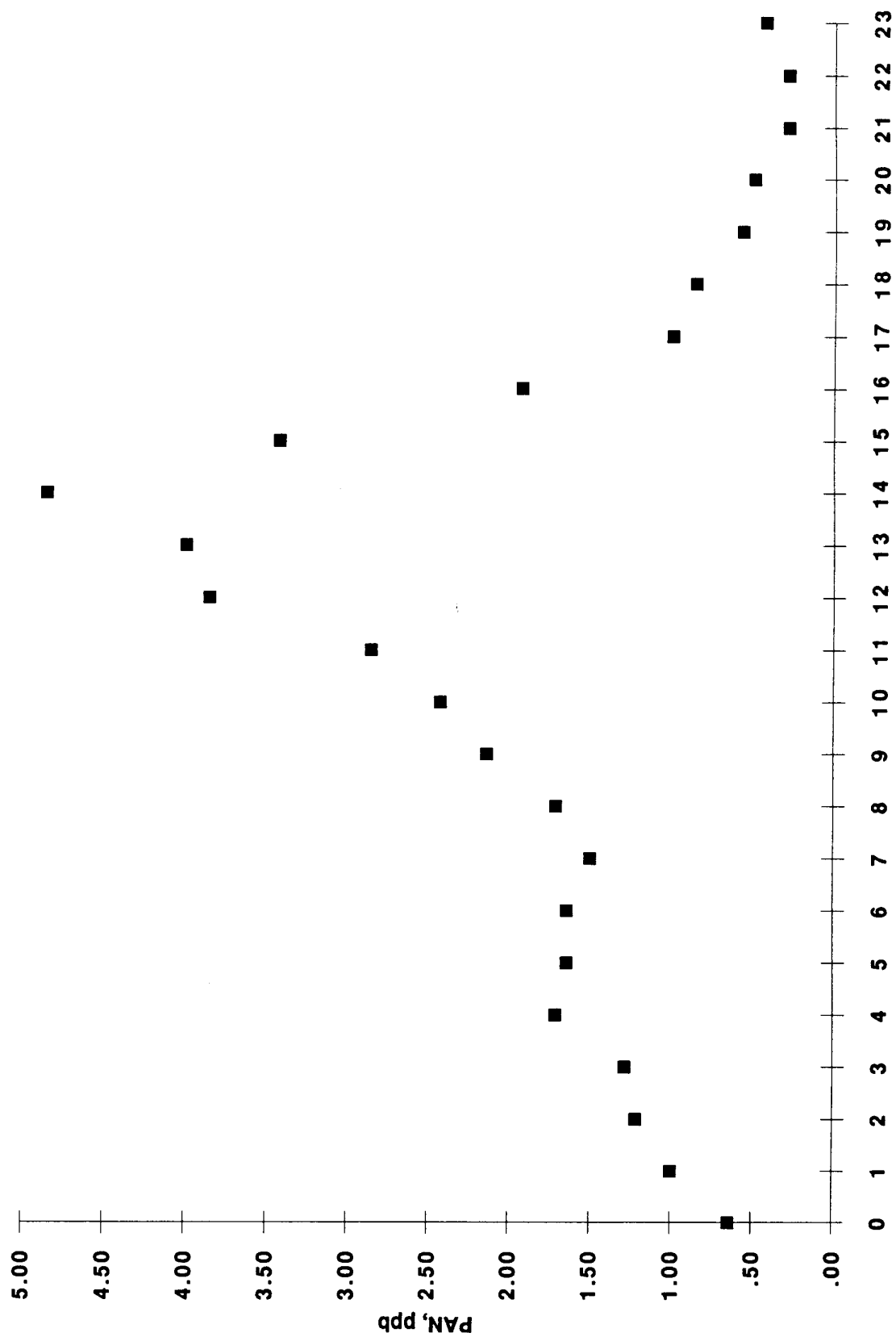
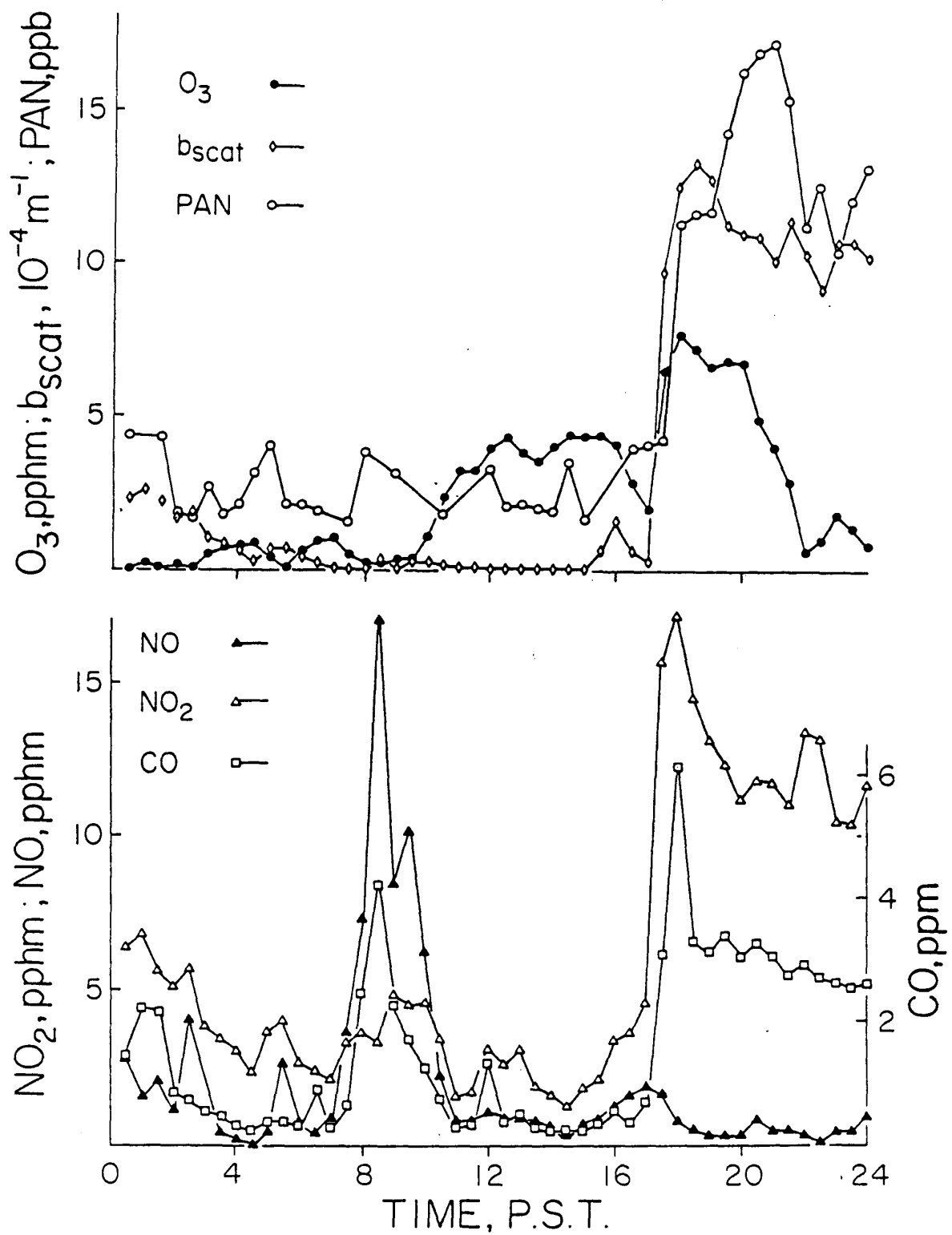


FIGURE 1(C)



Diurnal profile for NO,  $\text{NO}_2$ ,  $\text{O}_3$ , PAN,  $b_{\text{scat}}$ , and CO, February 16, 1977, Riverside, CA.

FIGURE 2

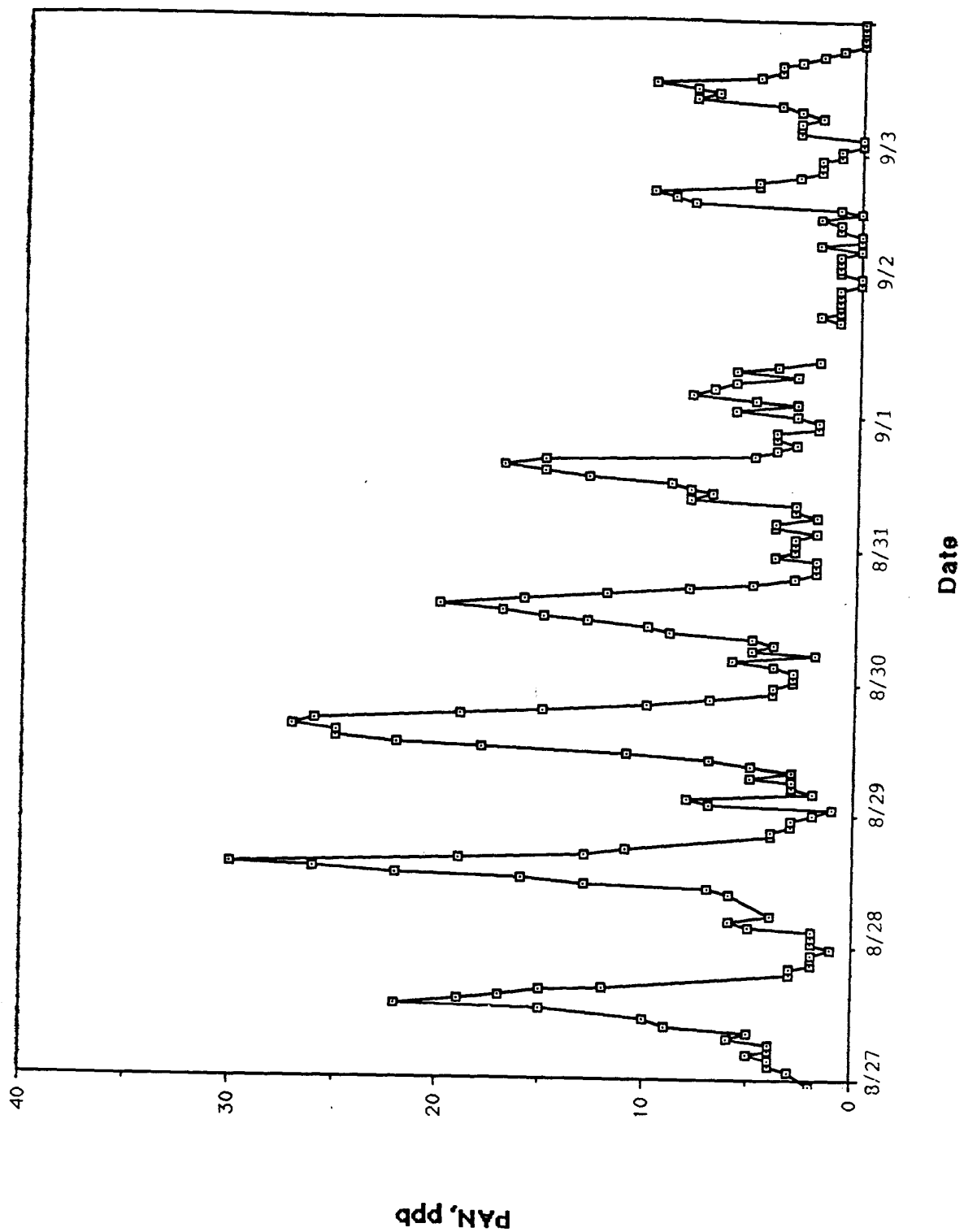
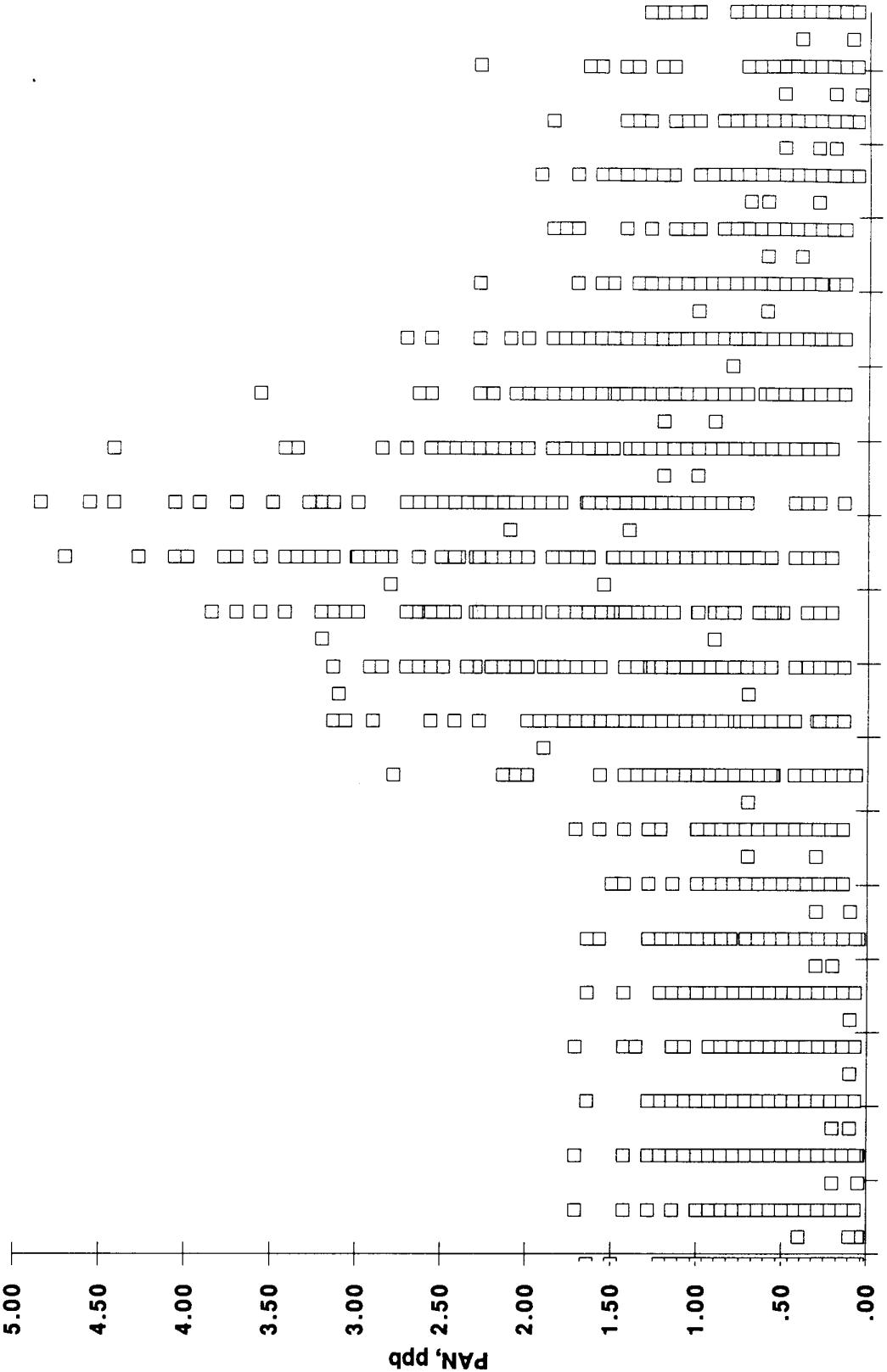


FIGURE 3

FIGURE 4

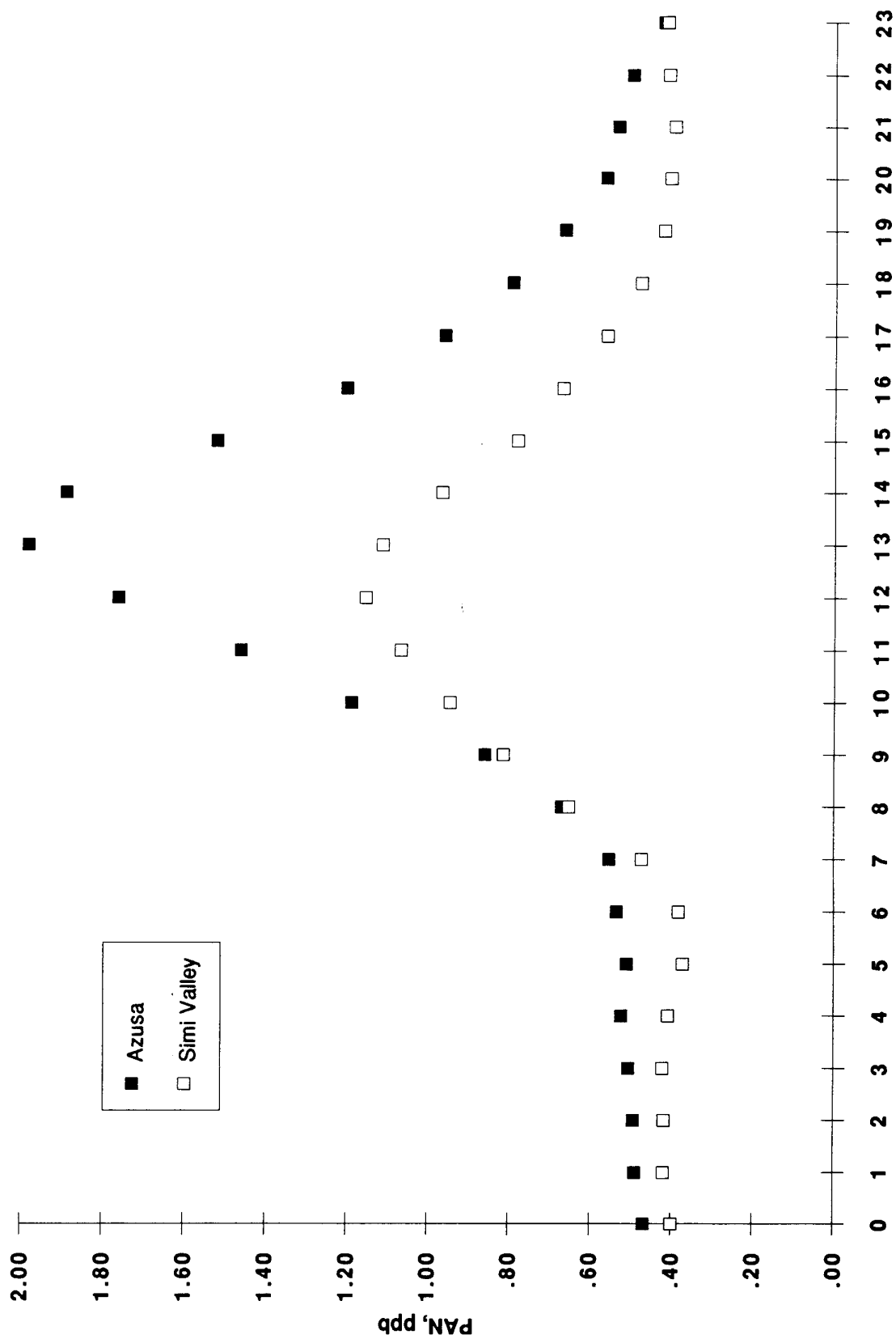
Azusa PAN ALL PST



0:40 2:02 3:24 4:45 6:07 7:28 8:50 10:12 11:33 12:55 14:16 15:38 17:00 18:21 19:43 21:04 22:26

FIGURE 5

PAN ALL PST



MAY, 1975 - OCT, 1975  
AVE DIURNAL PROFILE FOR PAN

○ PAN

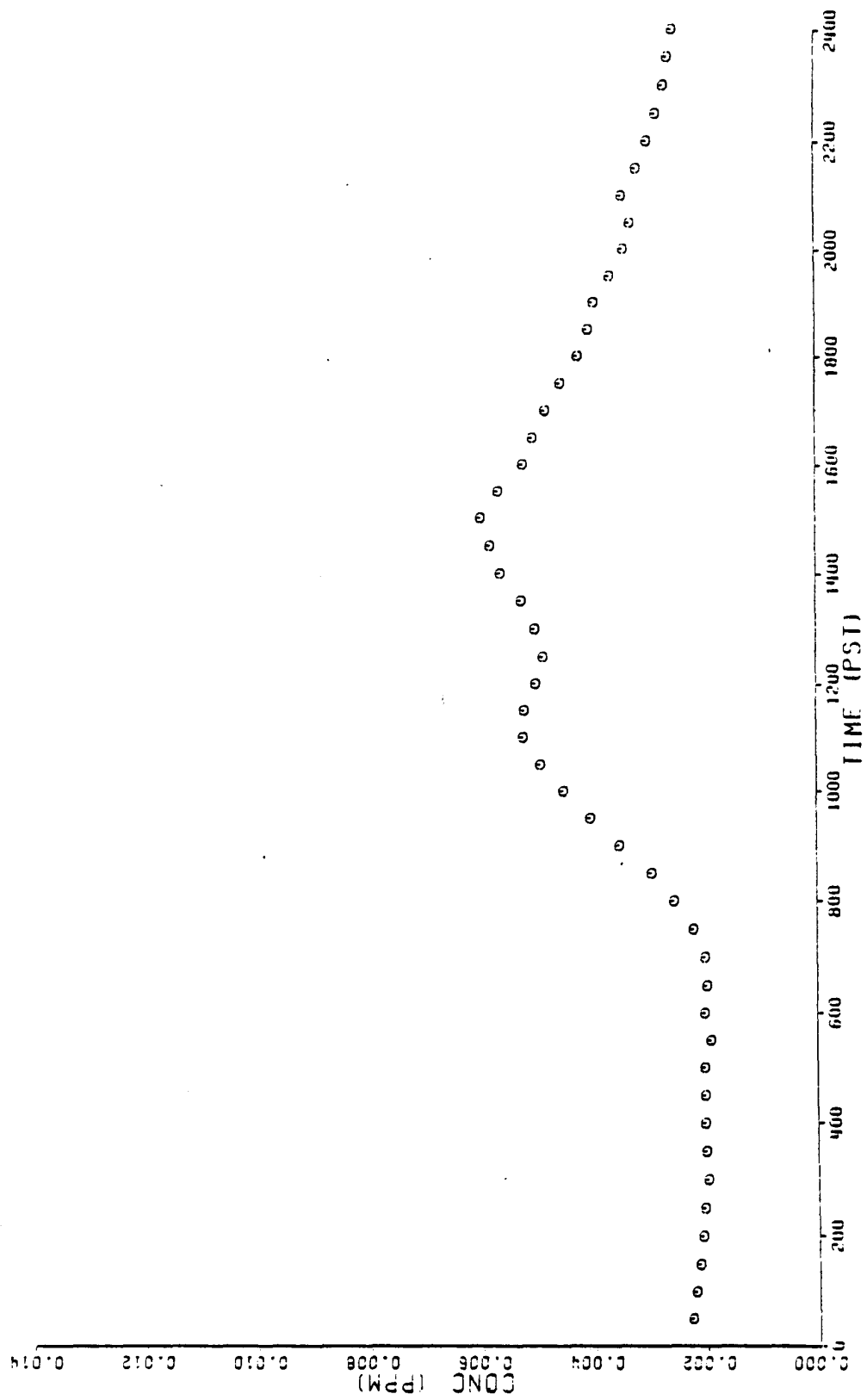


FIGURE 6(a)

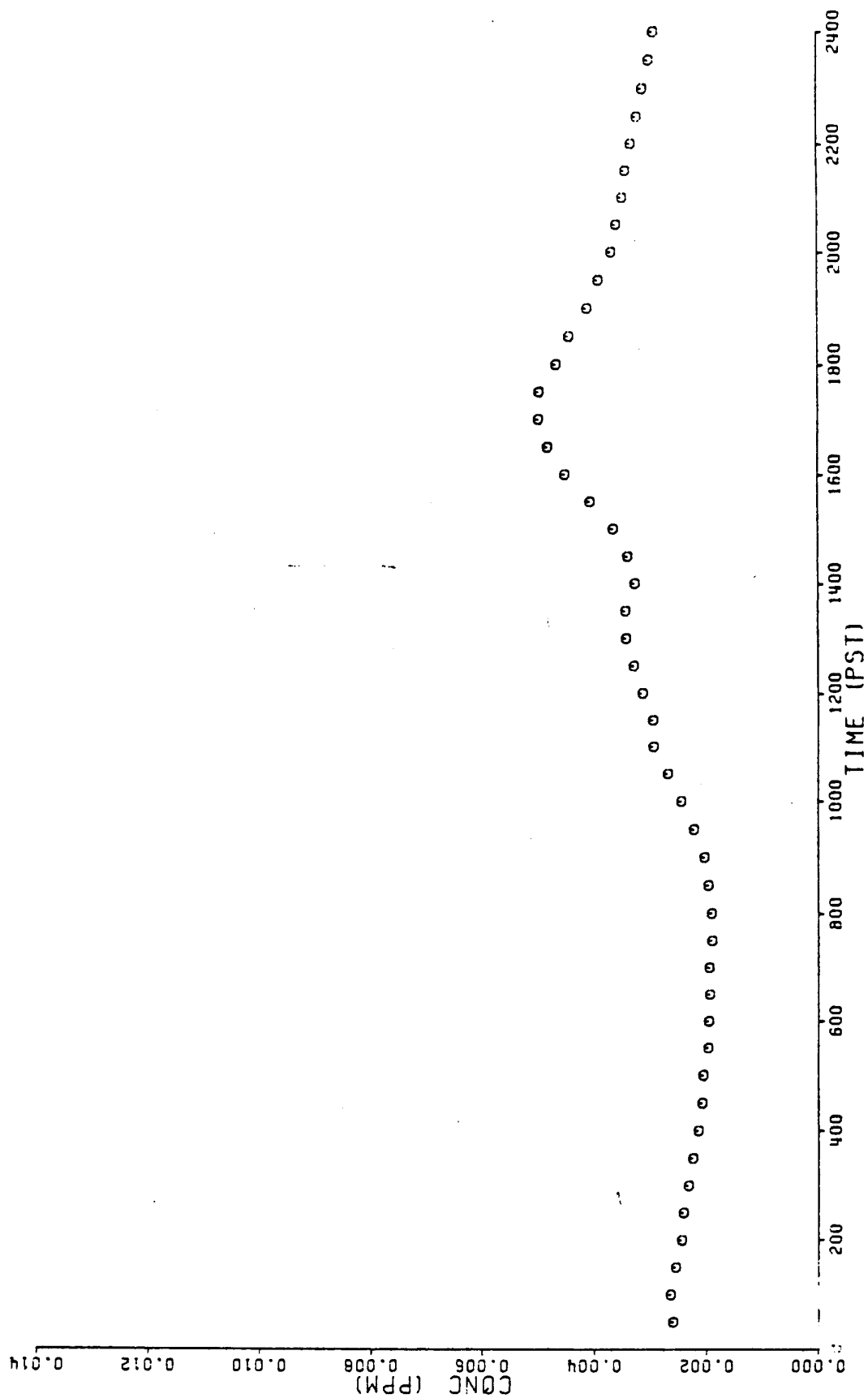


FIGURE 6(b)

MAY, 1976 - OCT, 1976  
AVE DIURNAL PROFILE FOR PAN

□ PAN

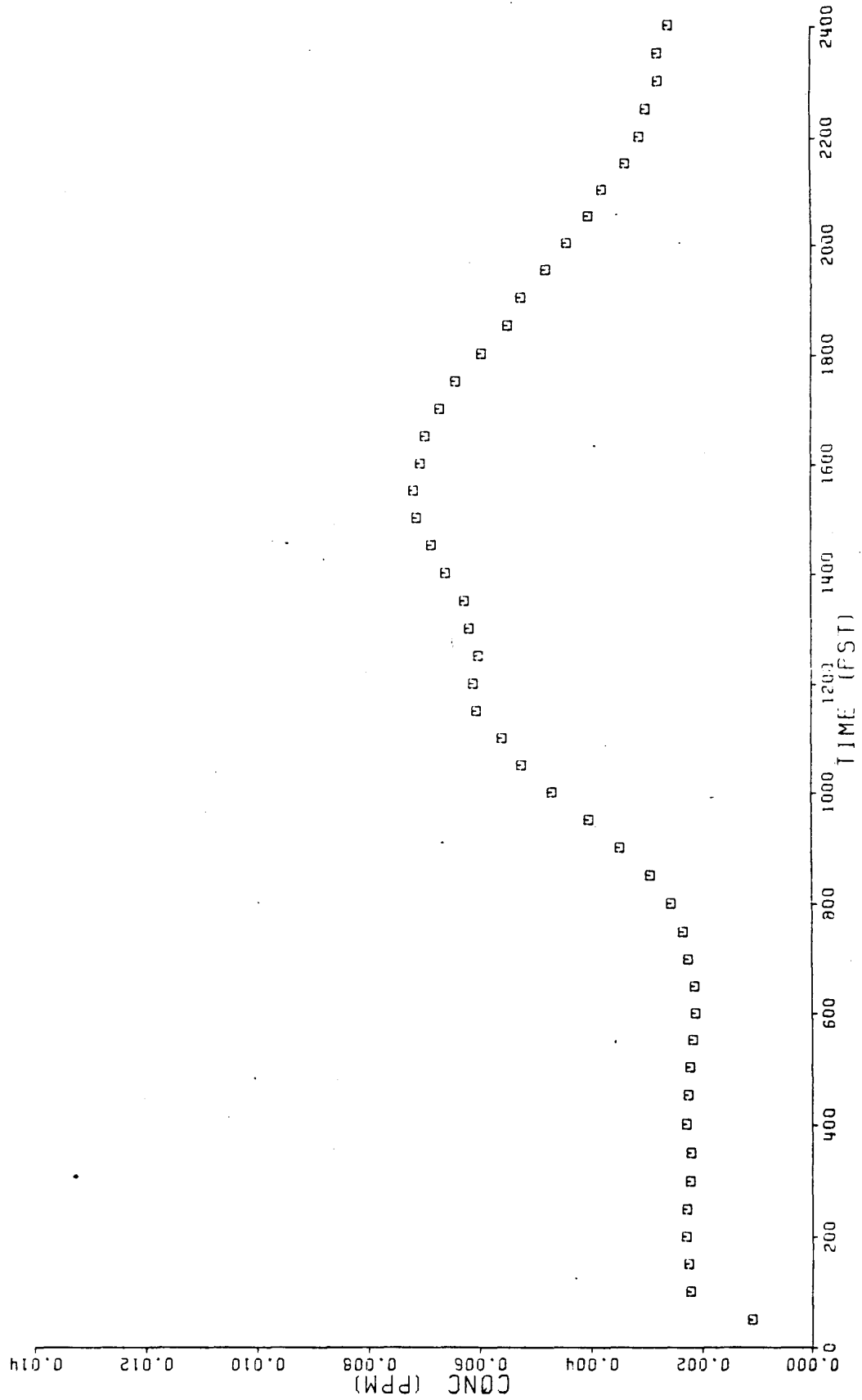


FIGURE 6(C)

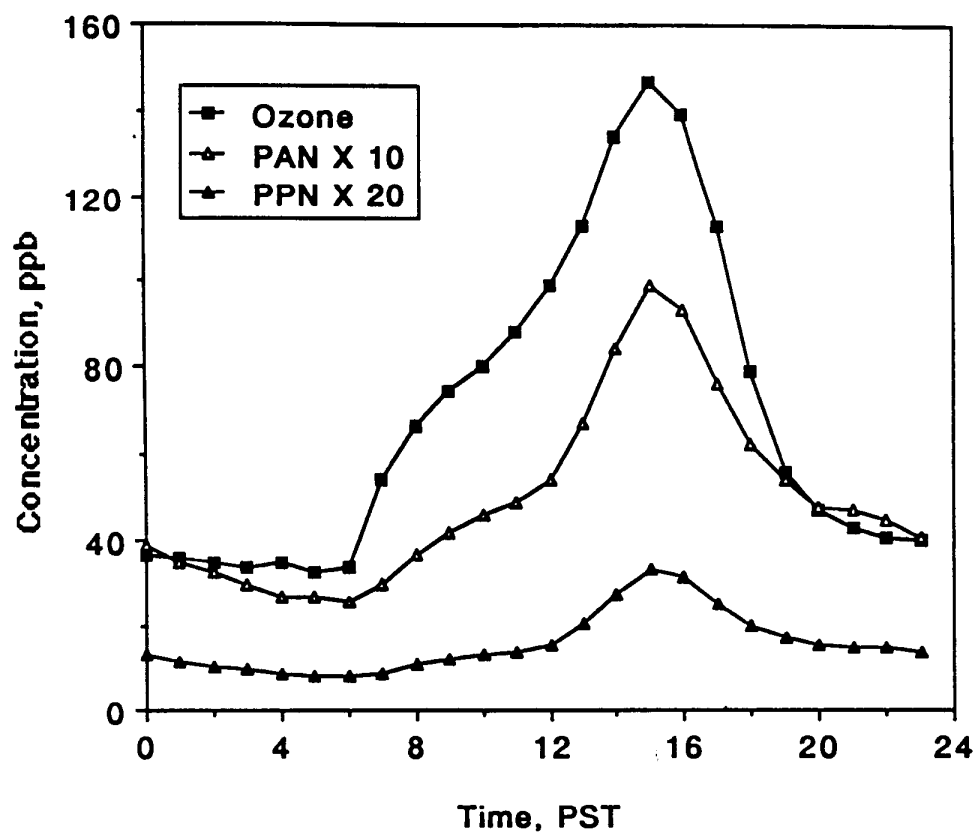


FIGURE 7(2)

Simi Valley, June 26, 1997

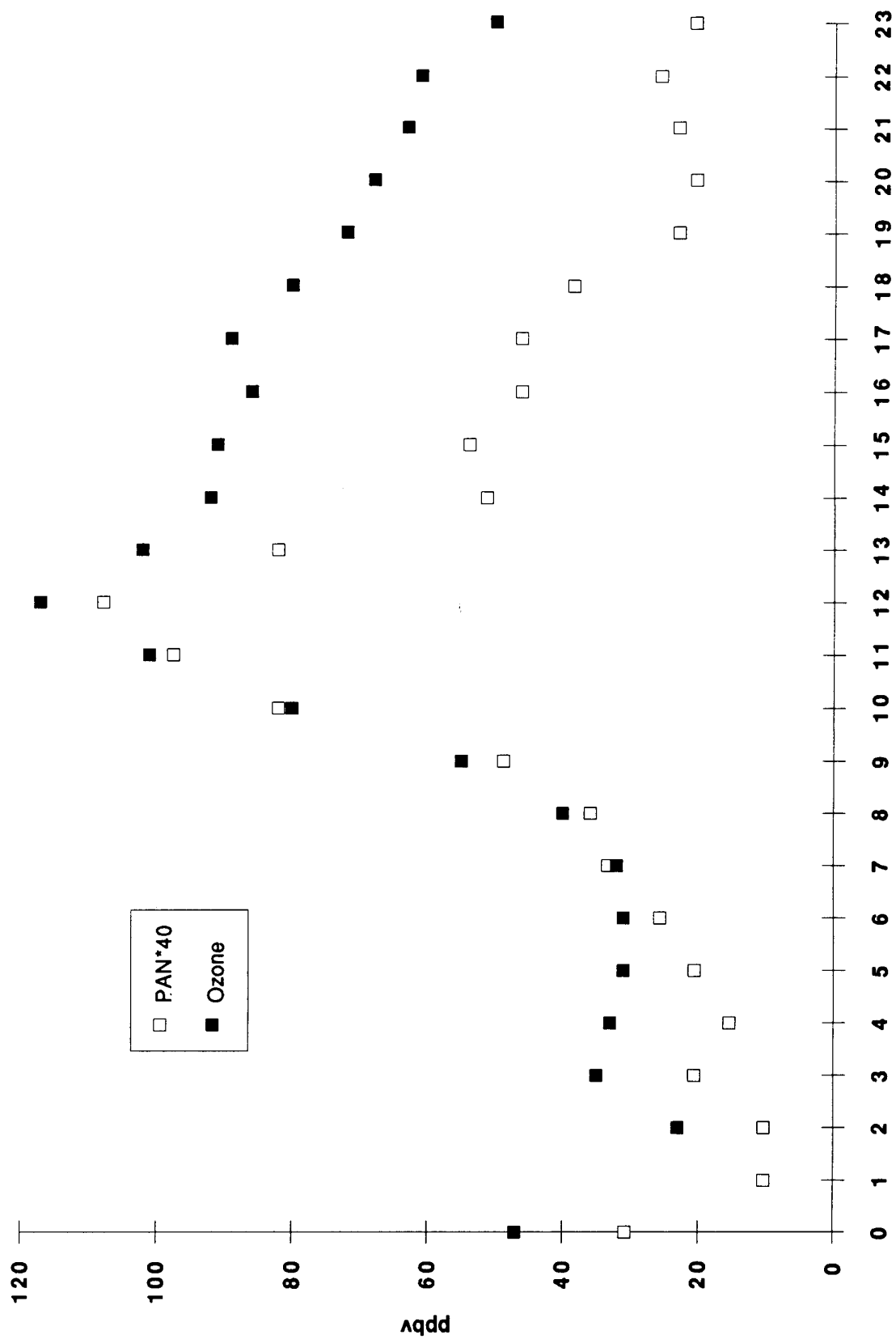


FIGURE 7(b)

Azusa, October 5, 1997

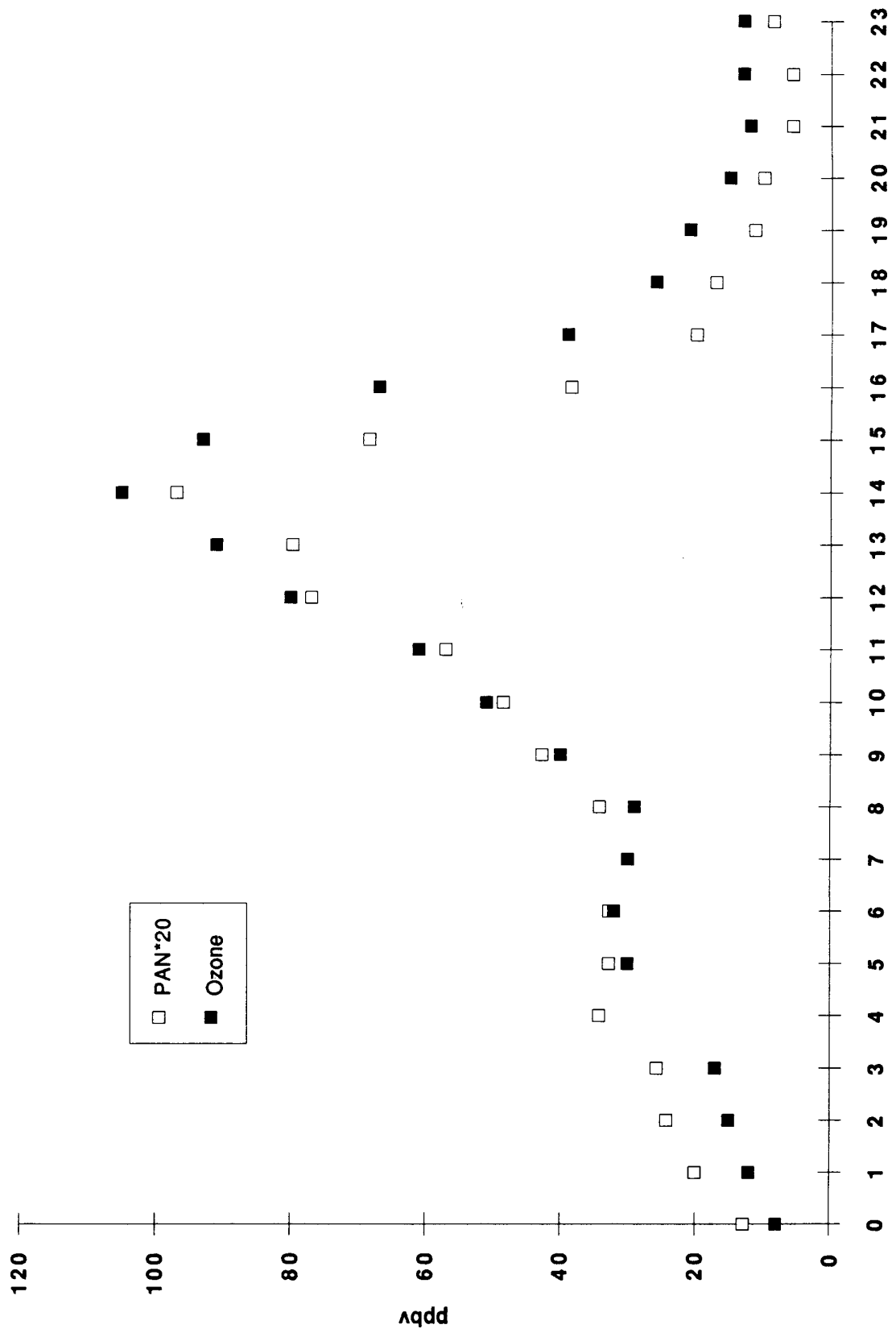


FIGURE 7(c)

Simi Valley ALL PST

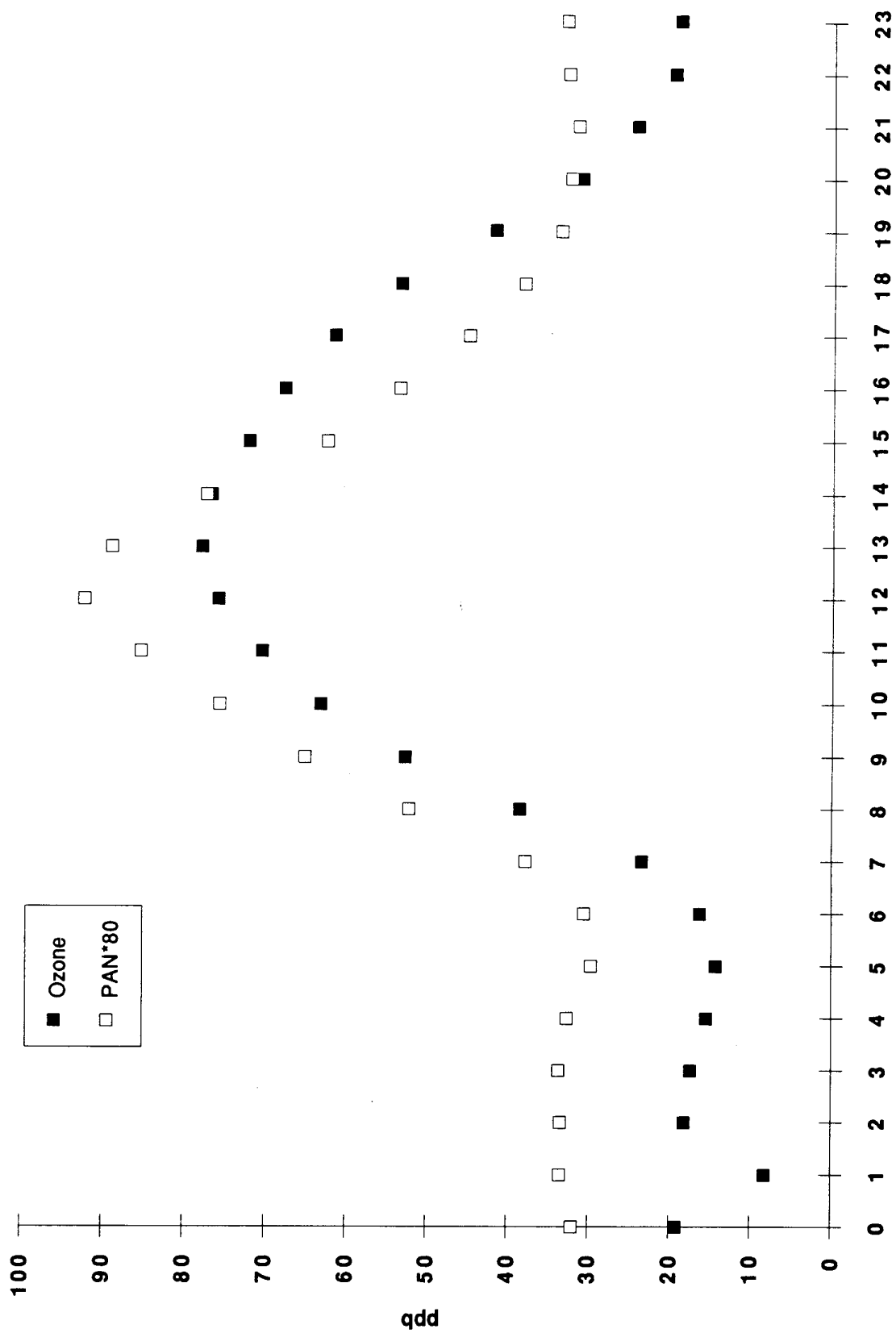


FIGURE 7(d)

Azusa ALL PST

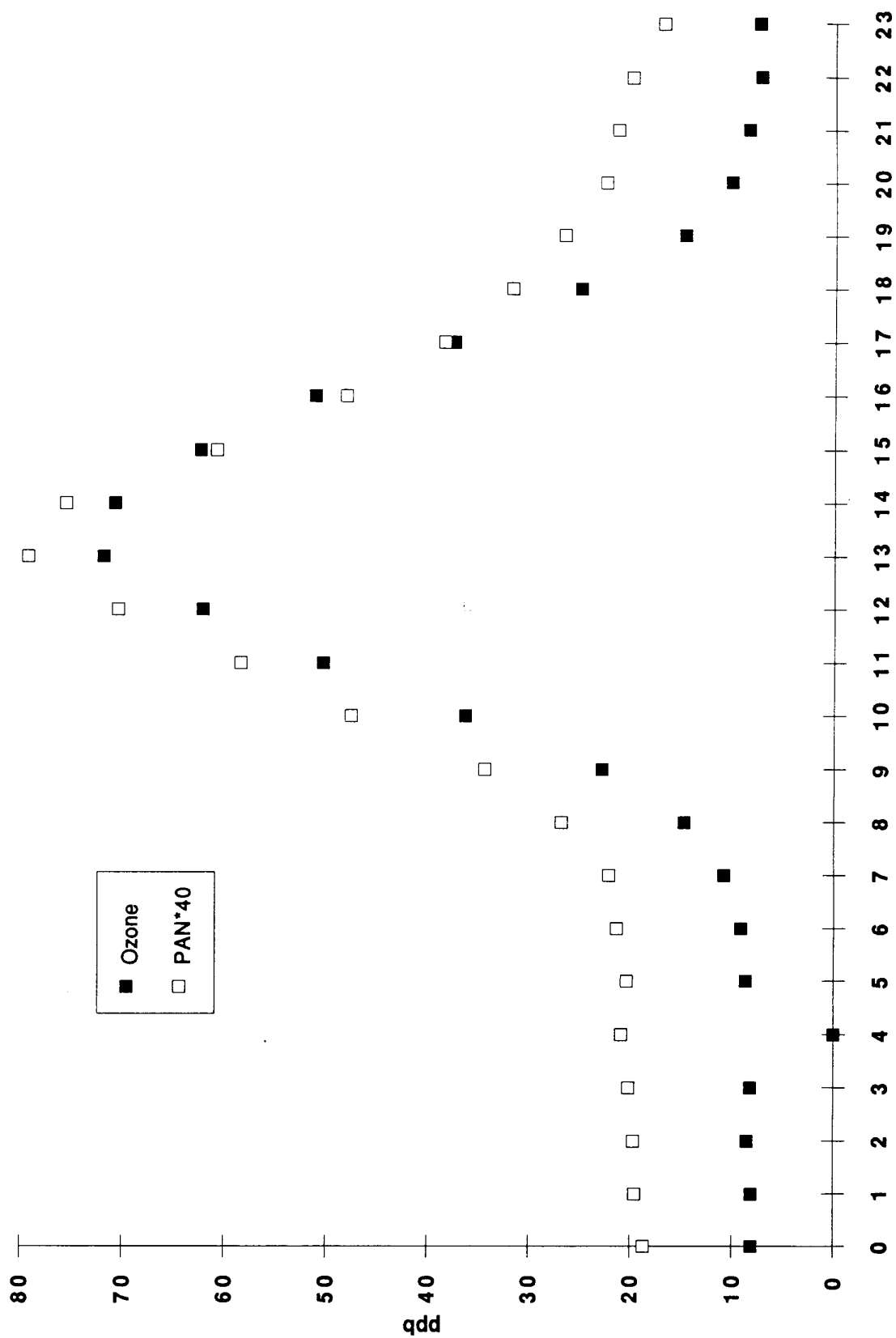
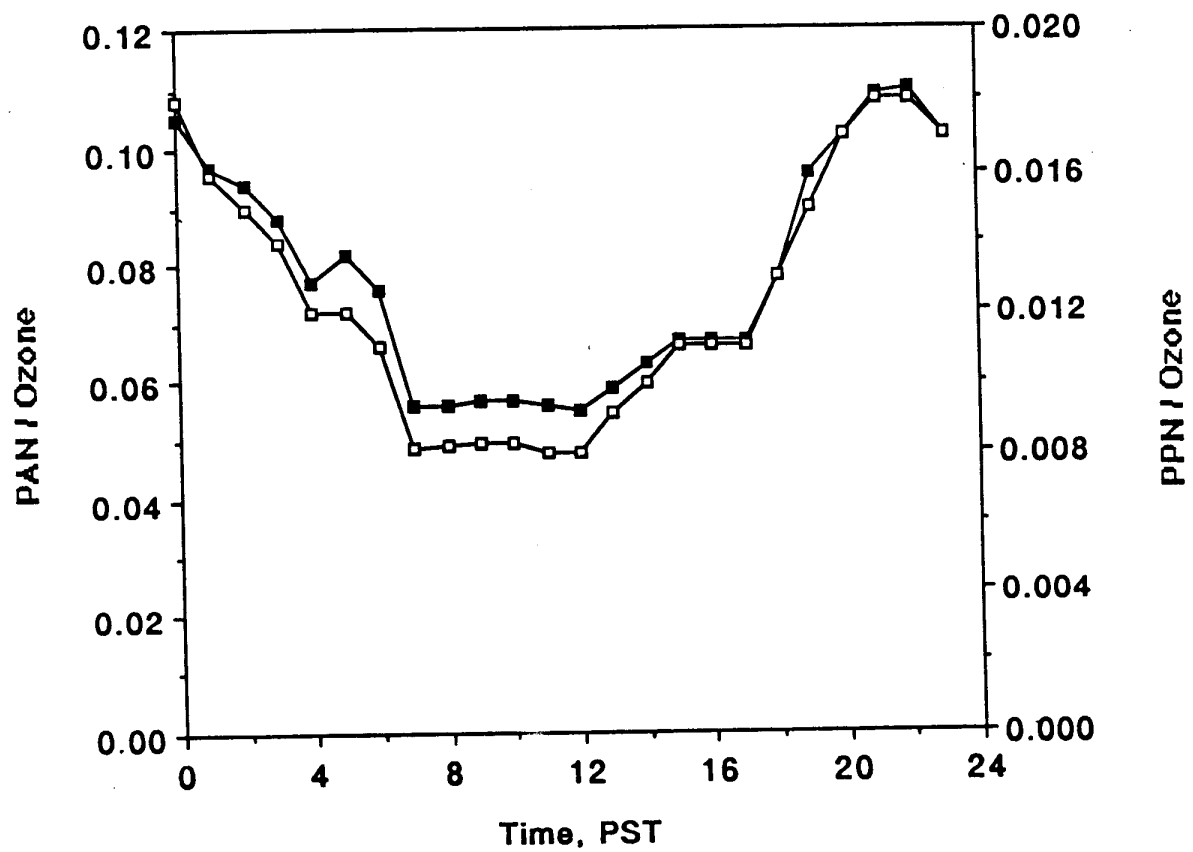


FIGURE 7(e)

FIGURE 8(a)



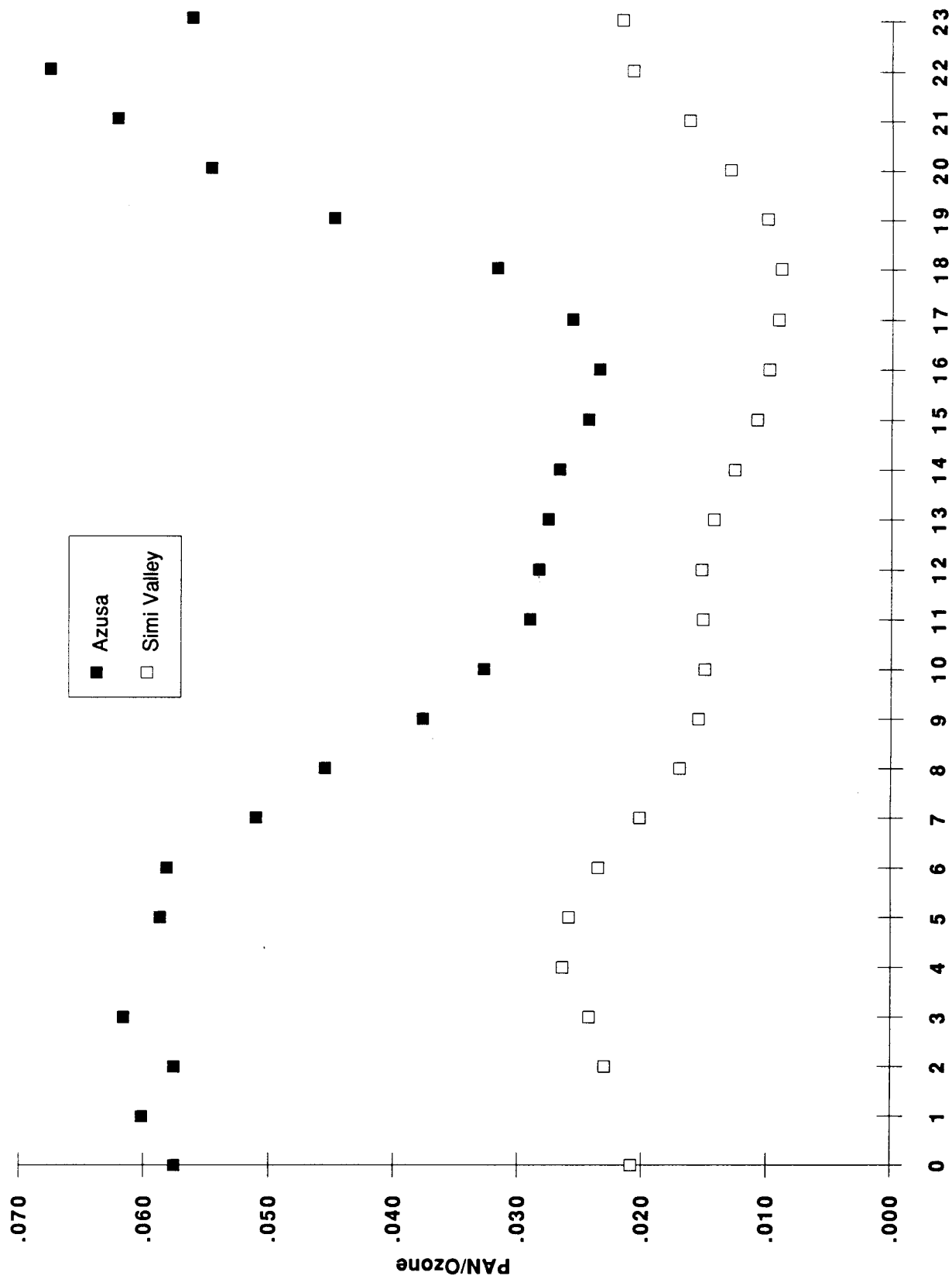


FIGURE 8(b)

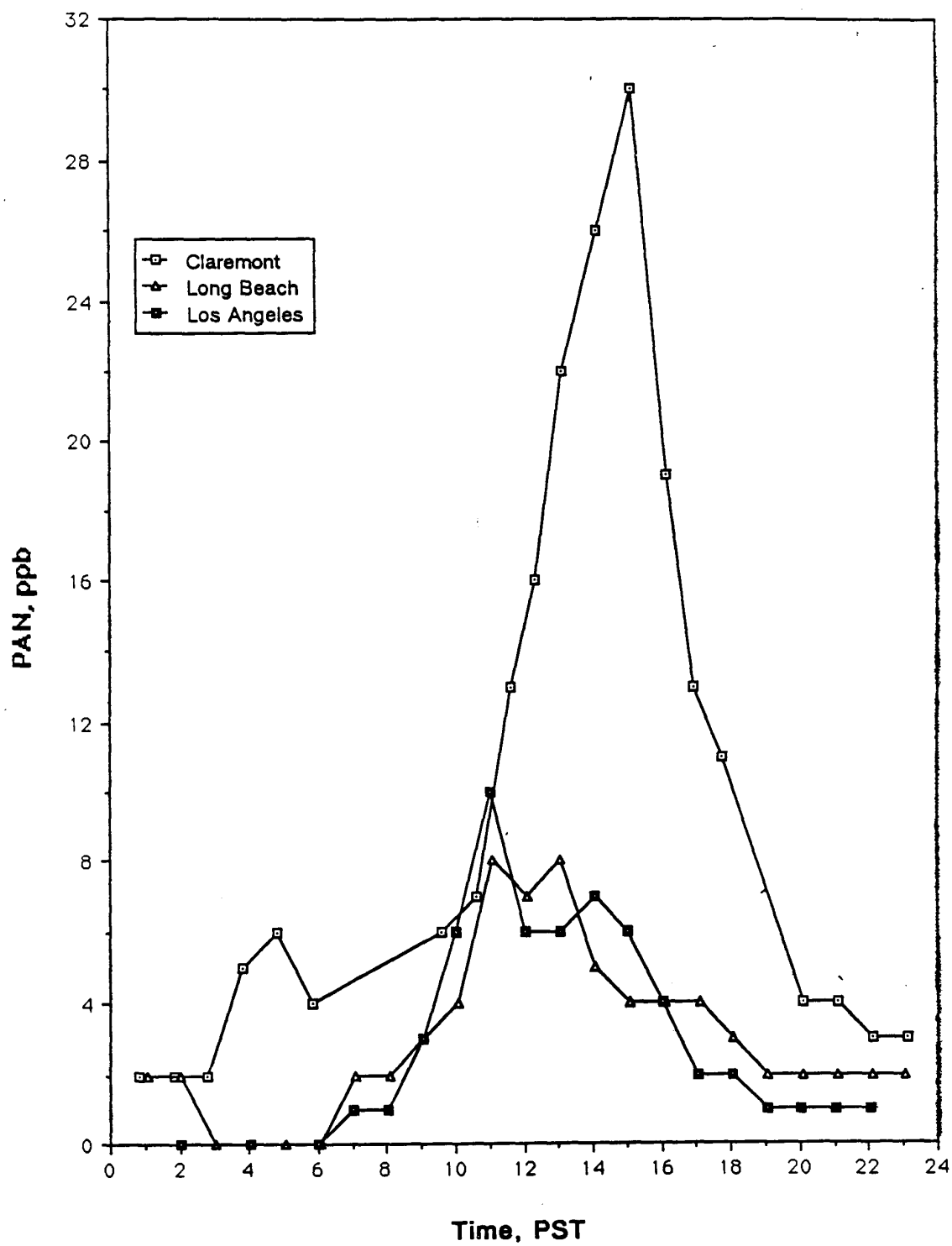
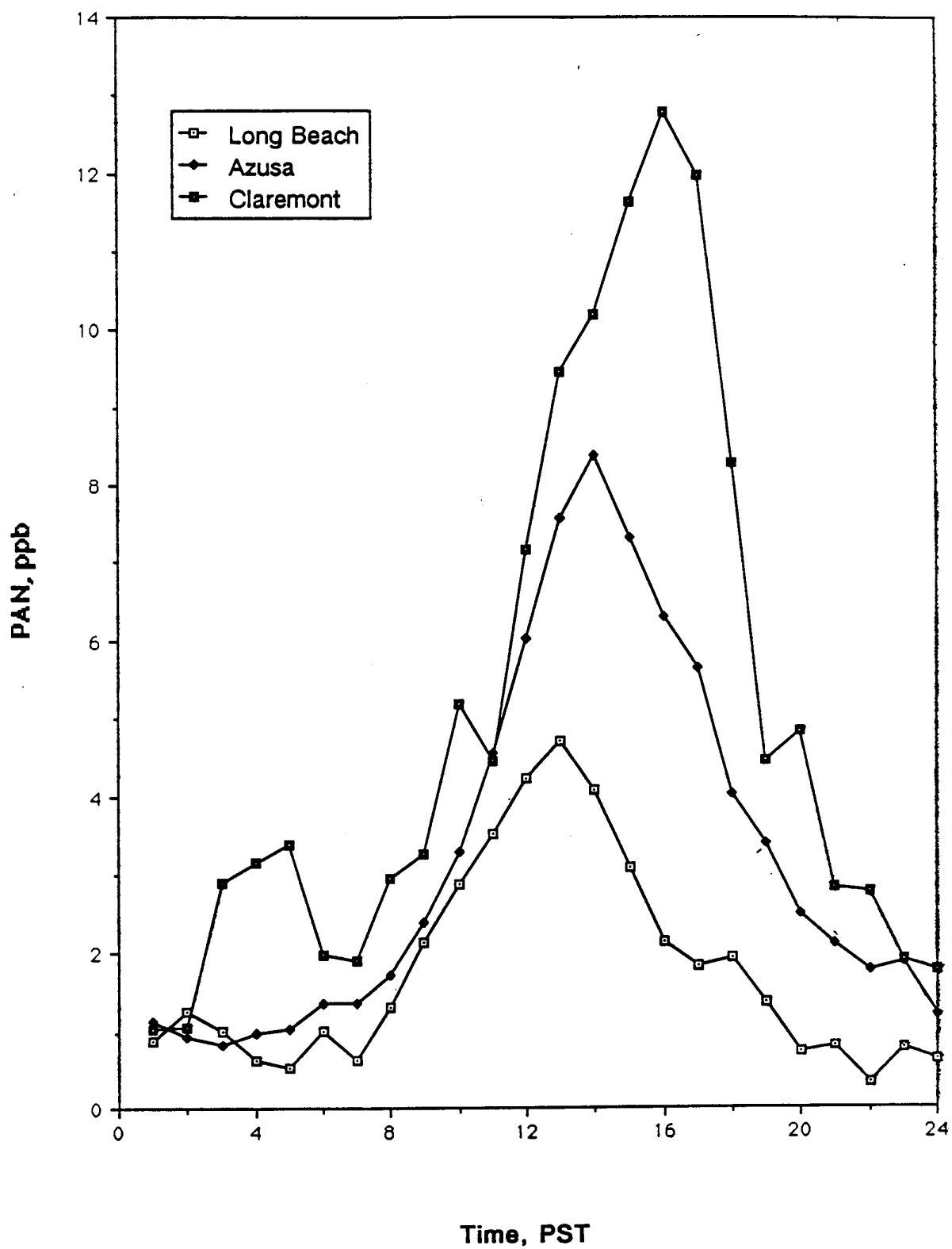


FIGURE 9

FIGURE 10



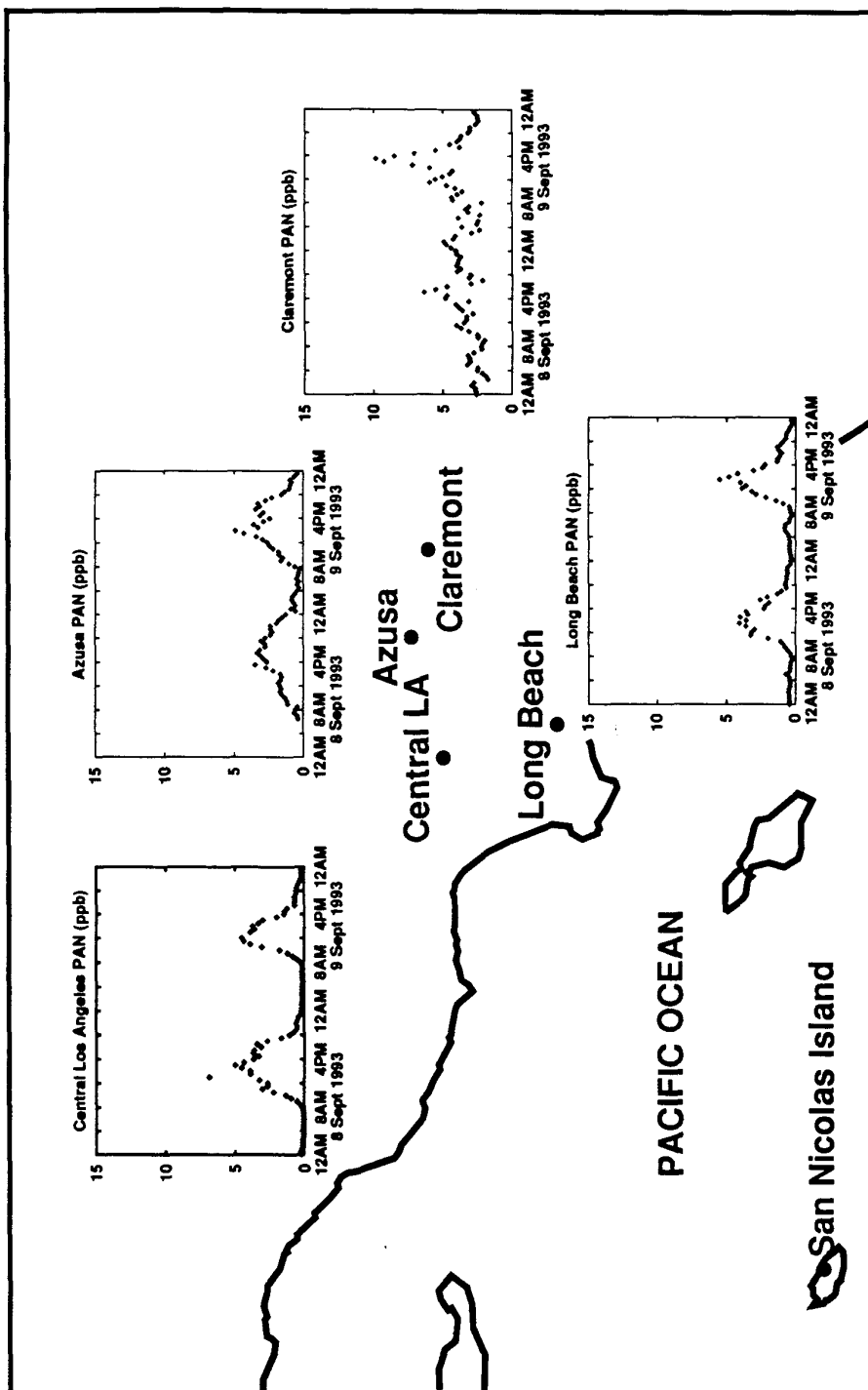


FIGURE 11

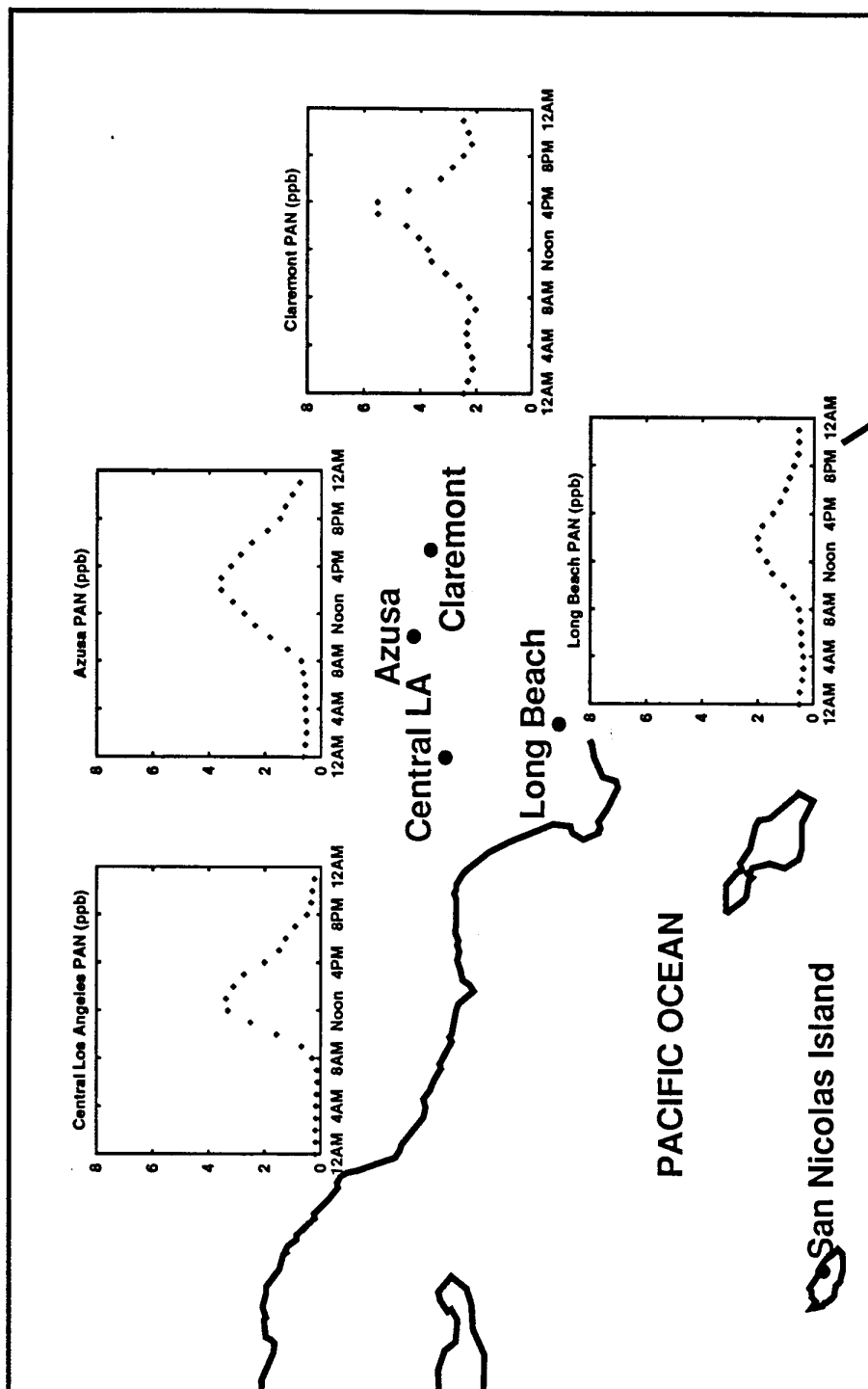


FIGURE 12

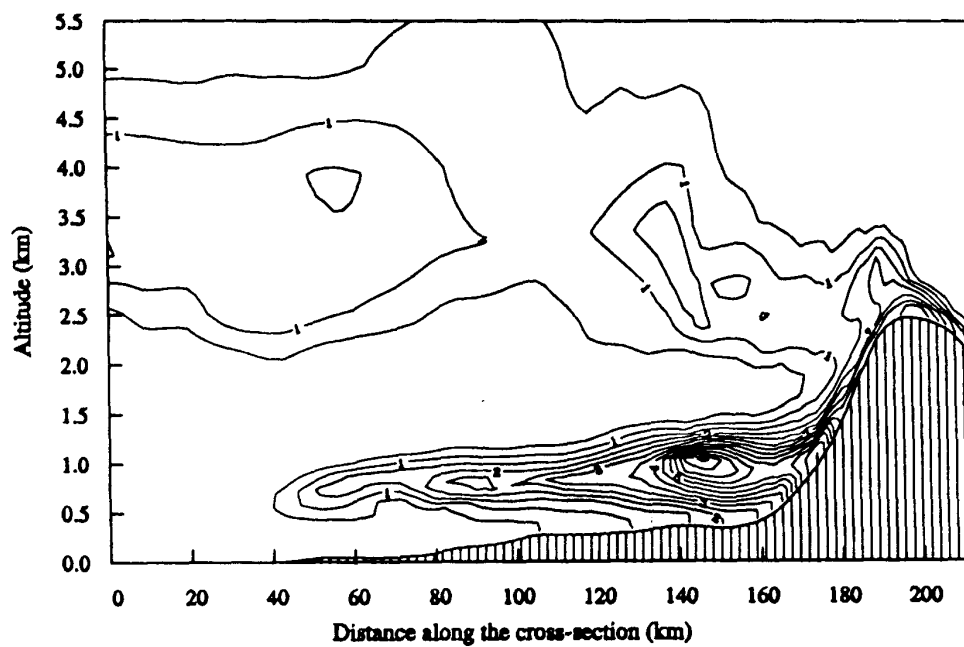


FIGURE 13

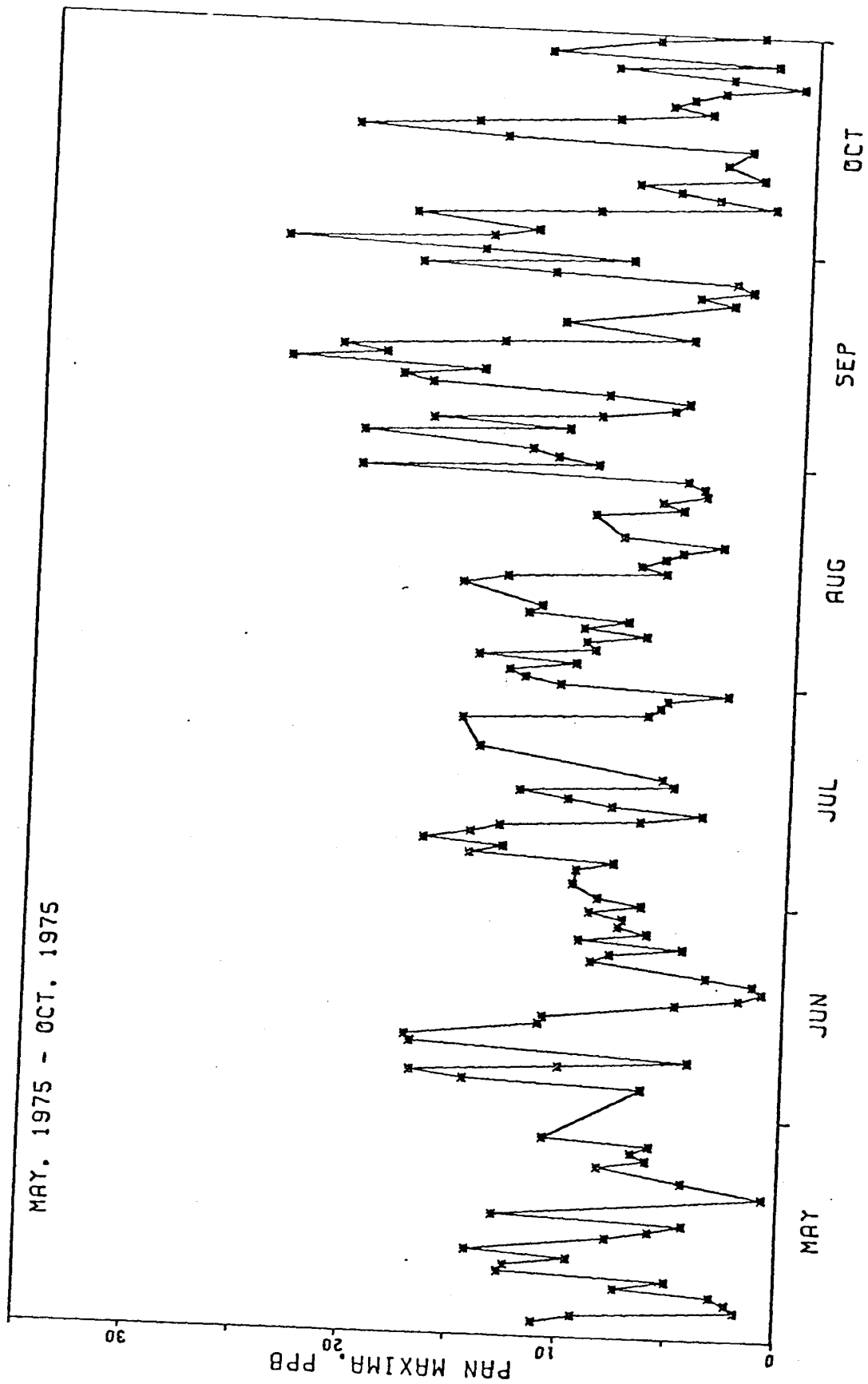


FIGURE 14(a)

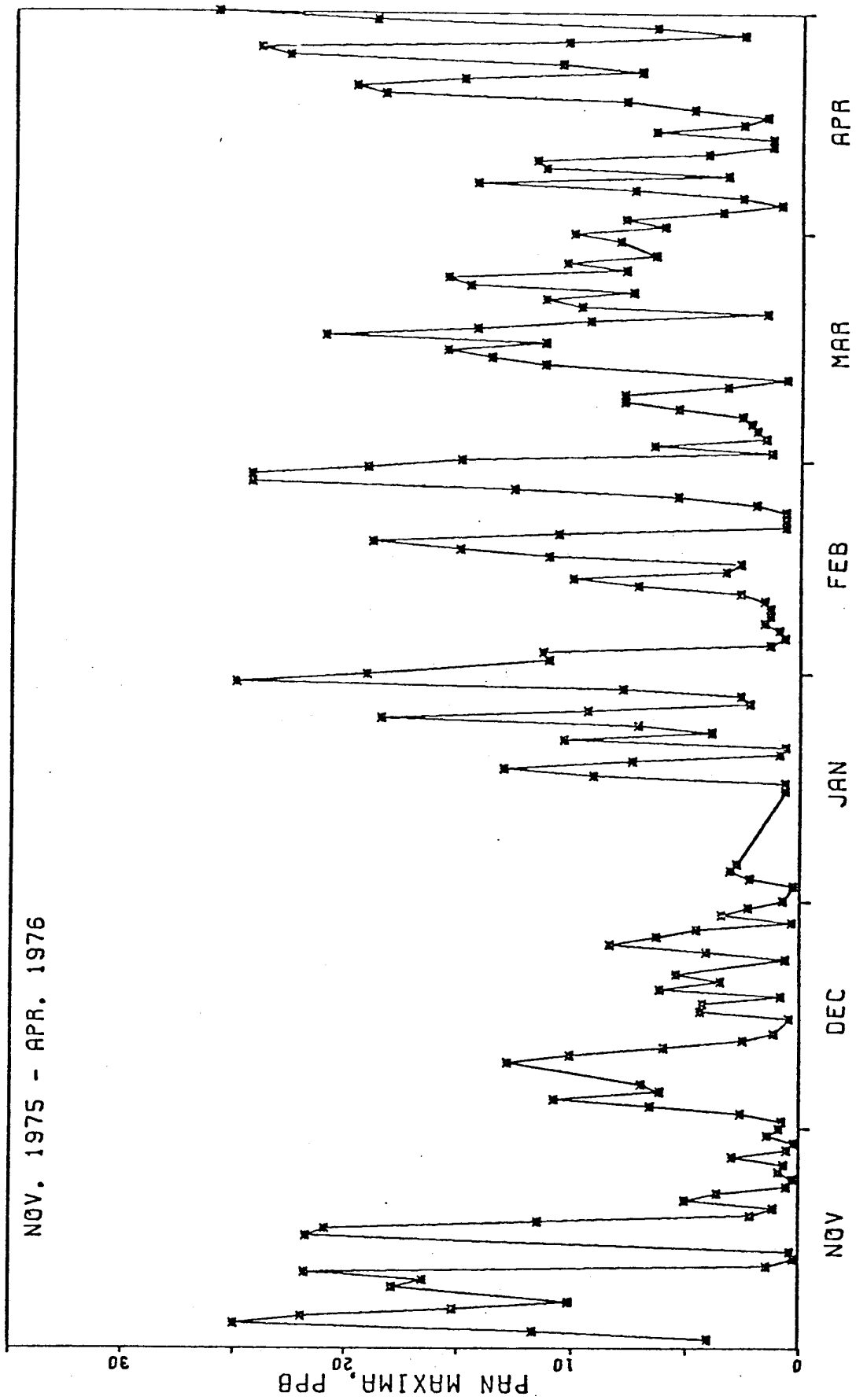


FIGURE 14 (b)

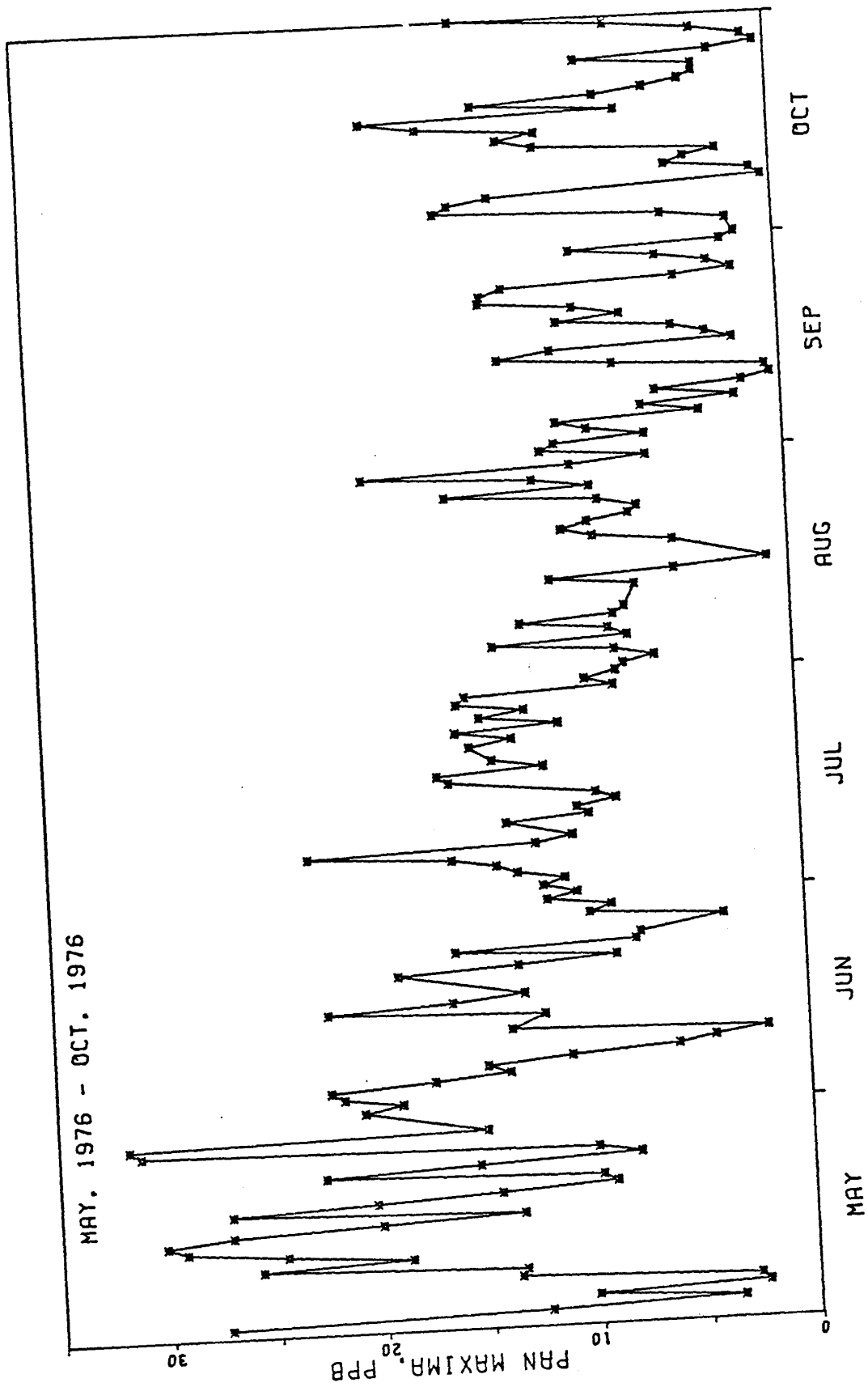


FIGURE 14(C)

FIGURE 15

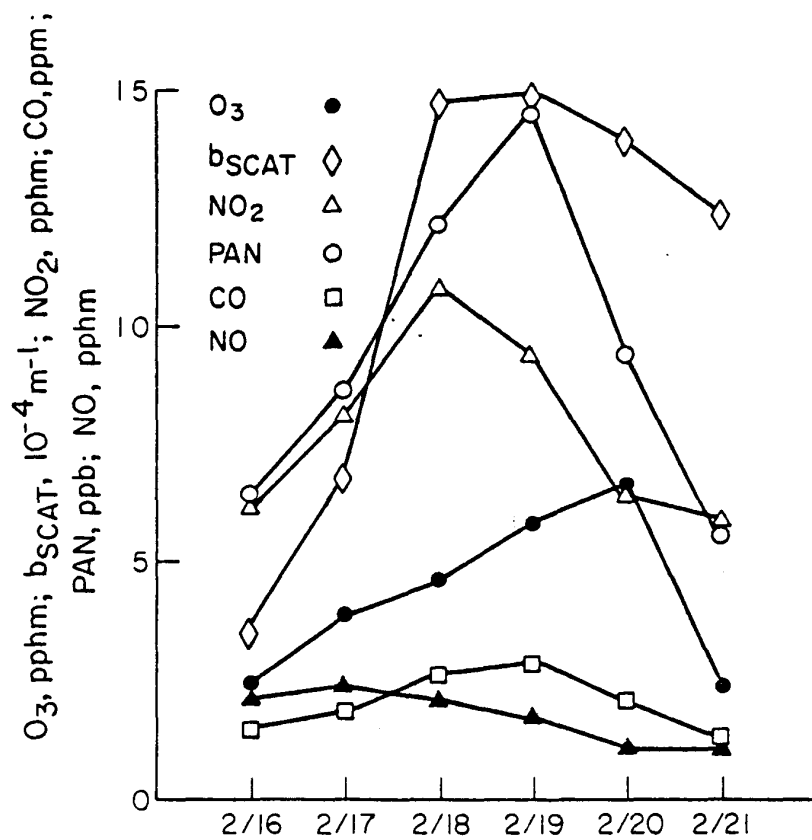


FIGURE 16

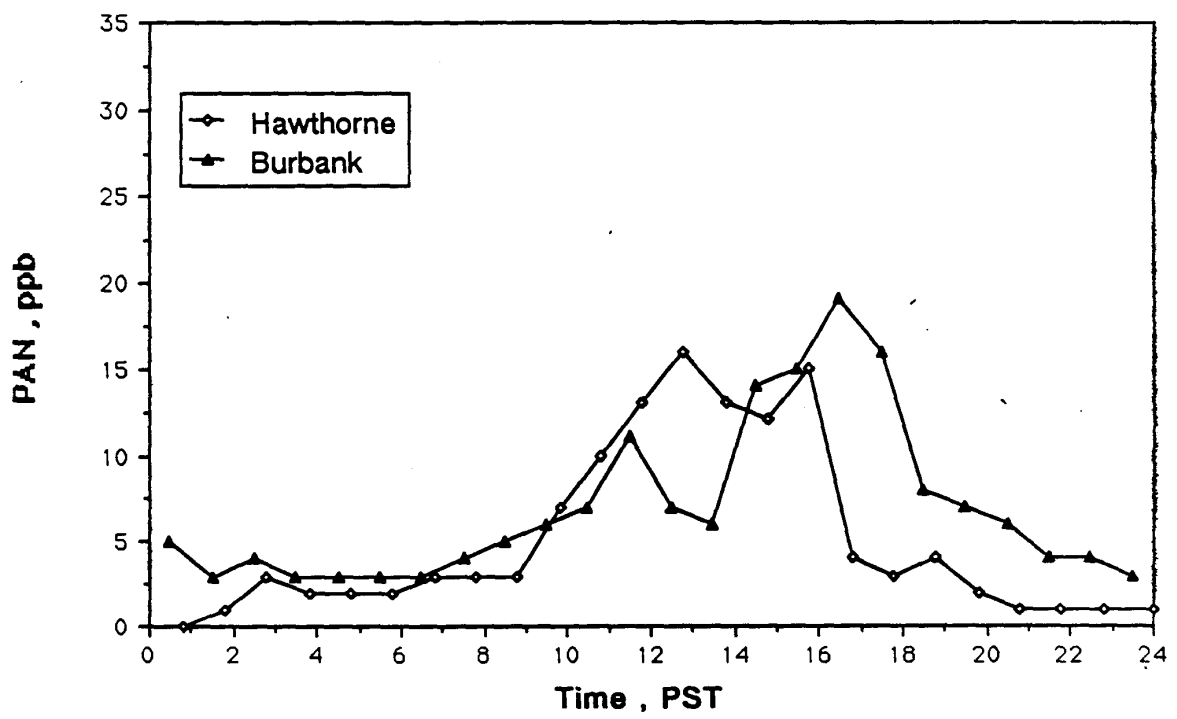
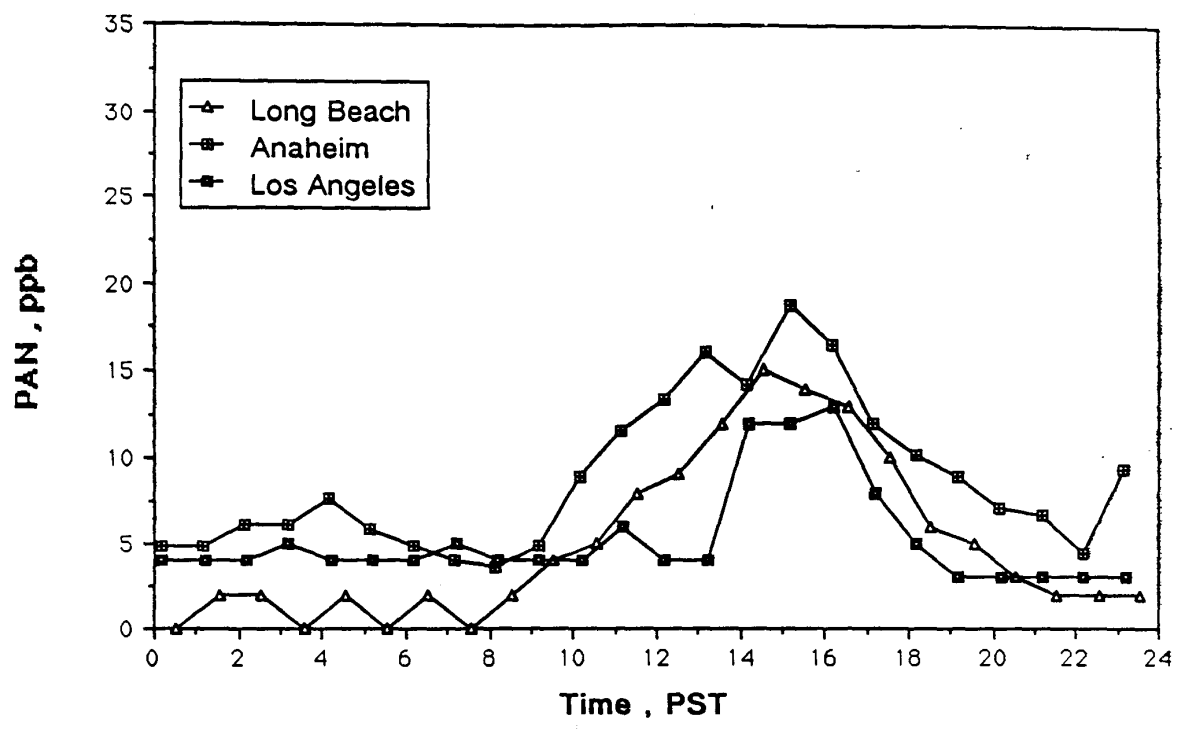


FIGURE 17

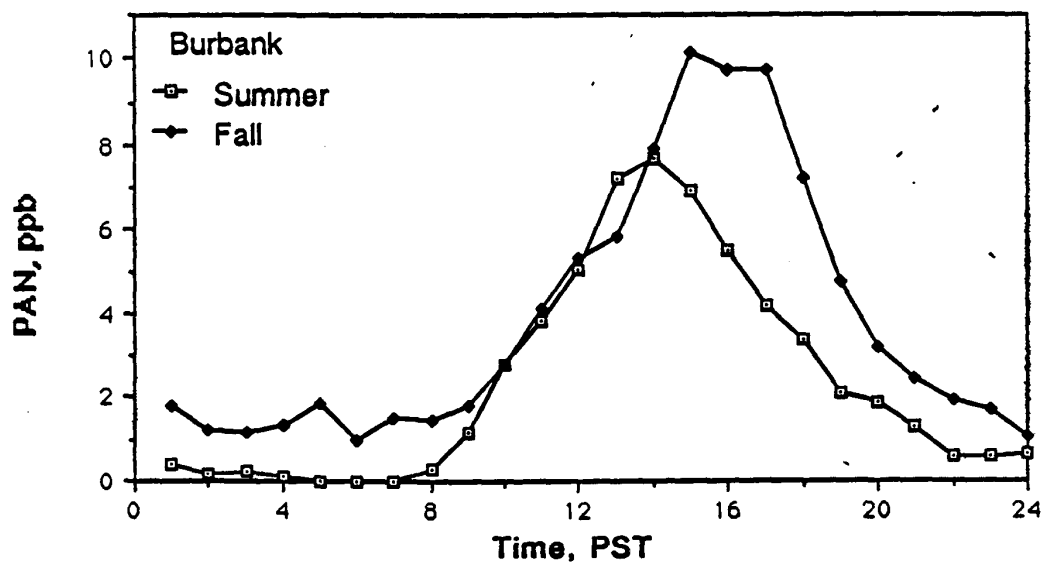
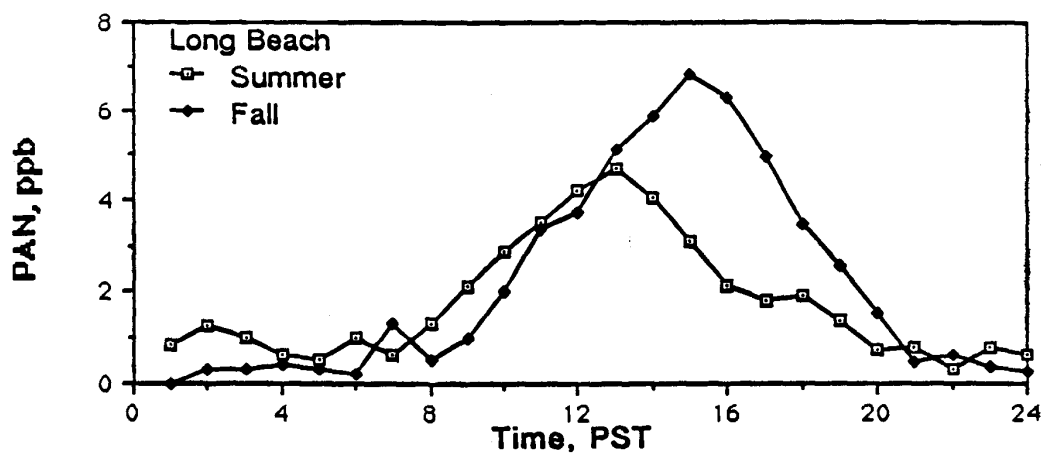
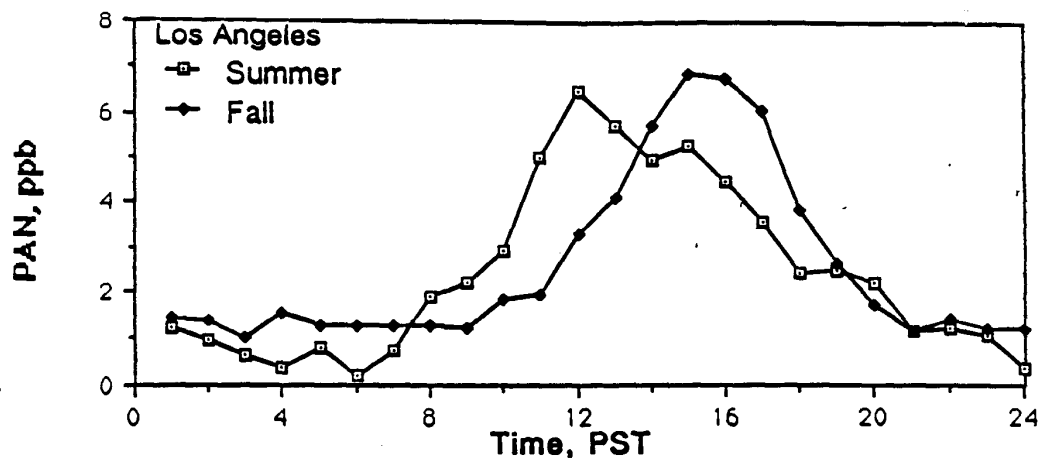


FIGURE 18

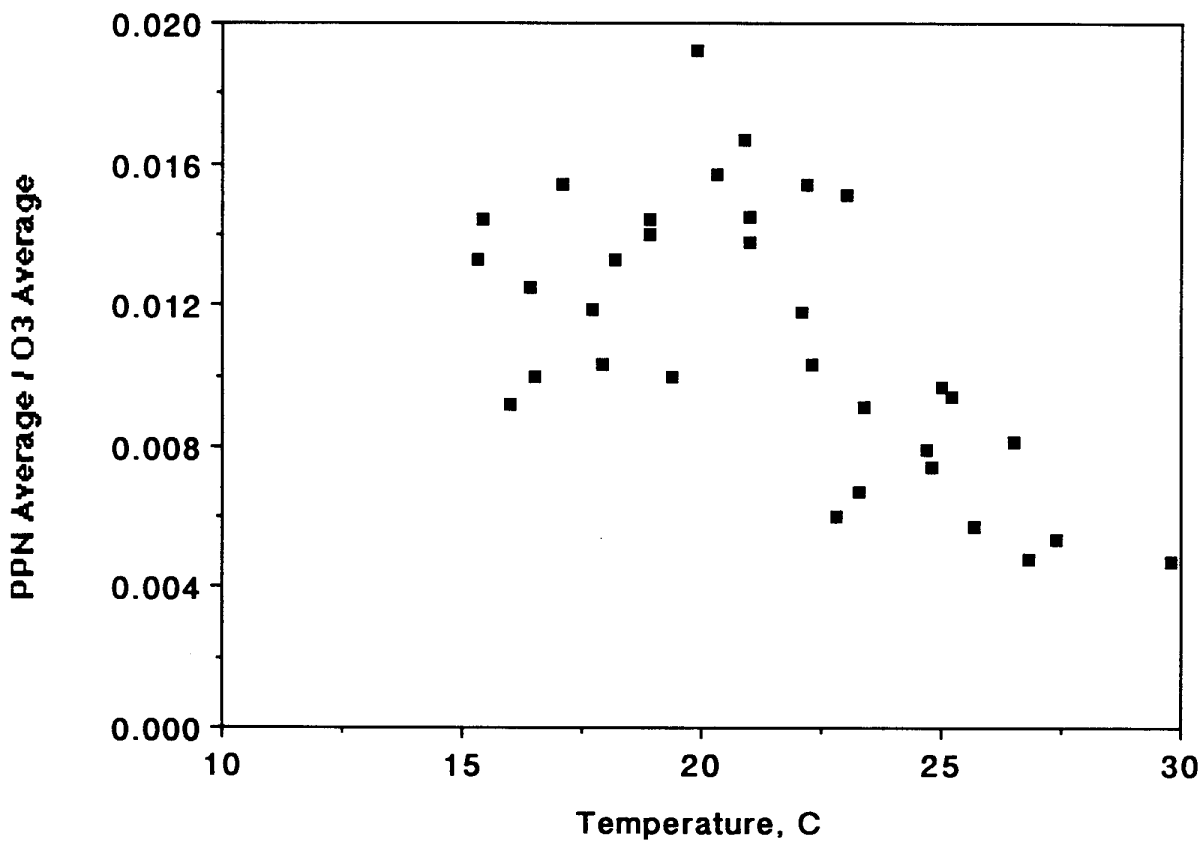
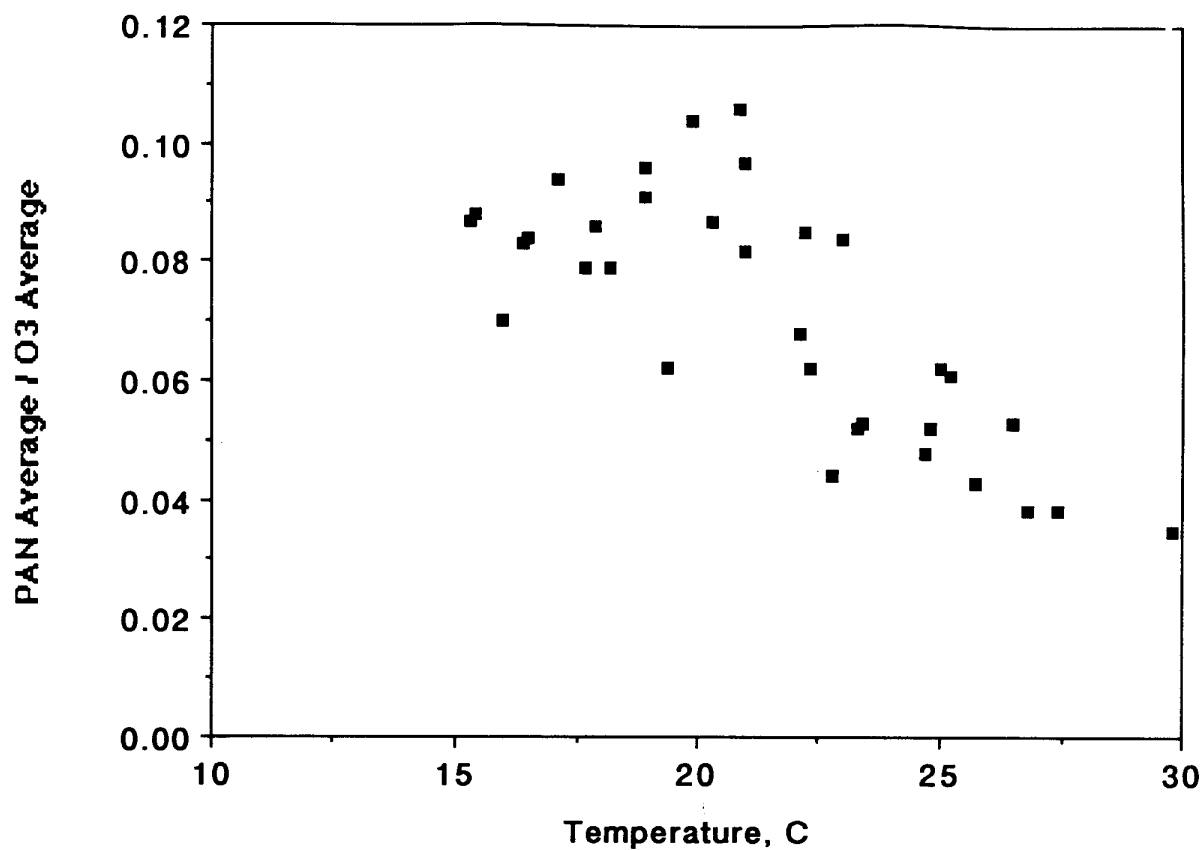


FIGURE 19 (a)

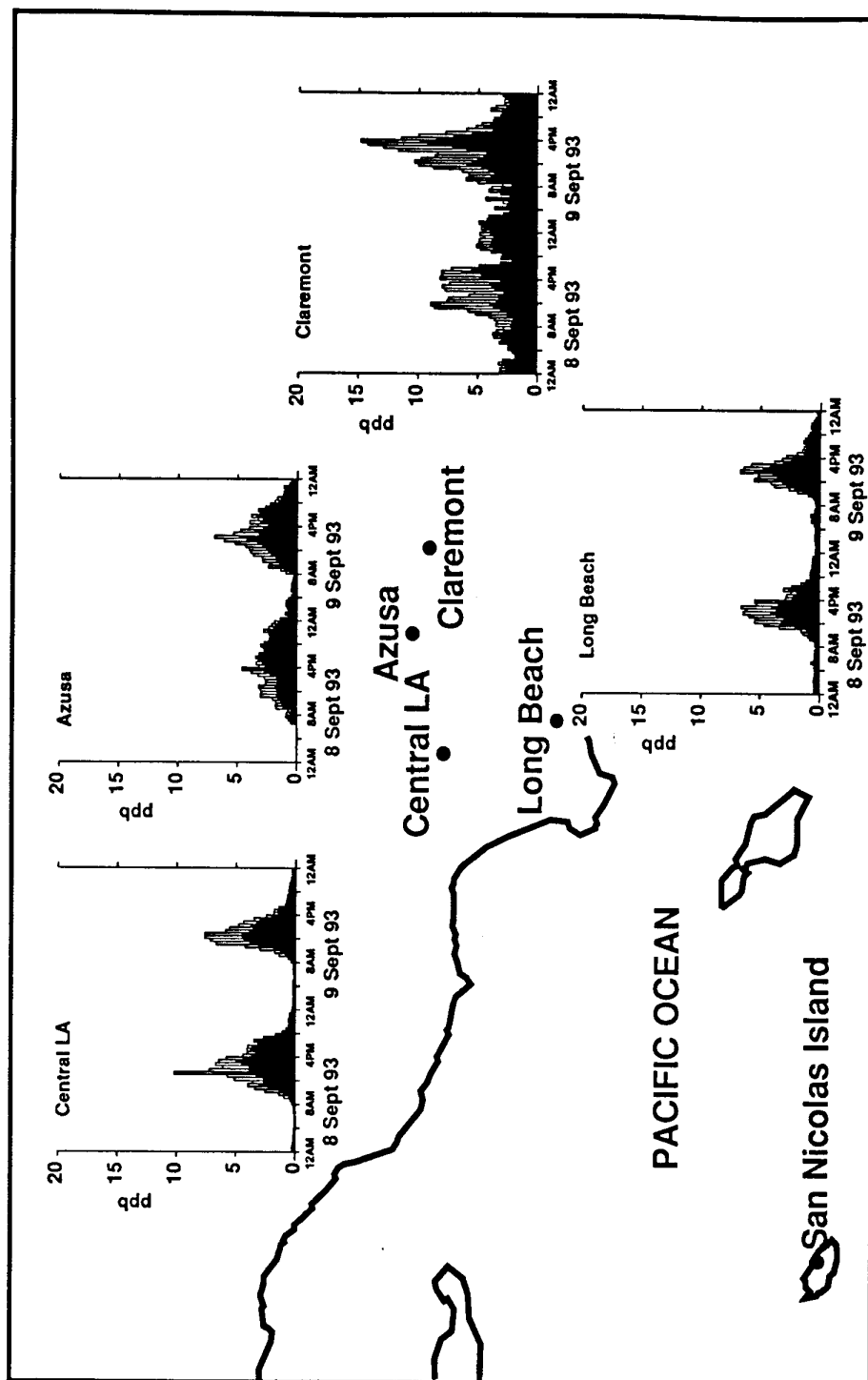


FIGURE 19(b)

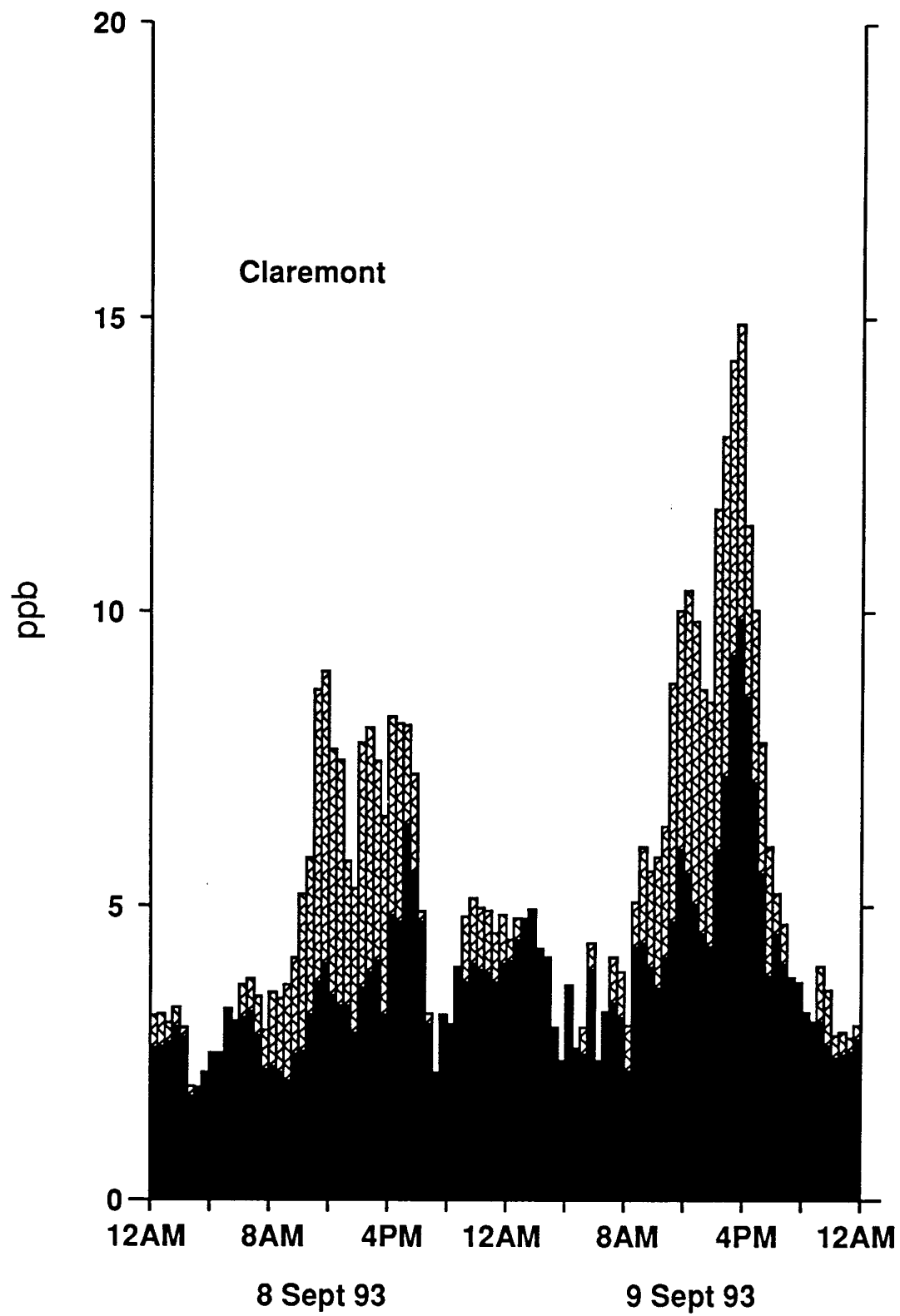
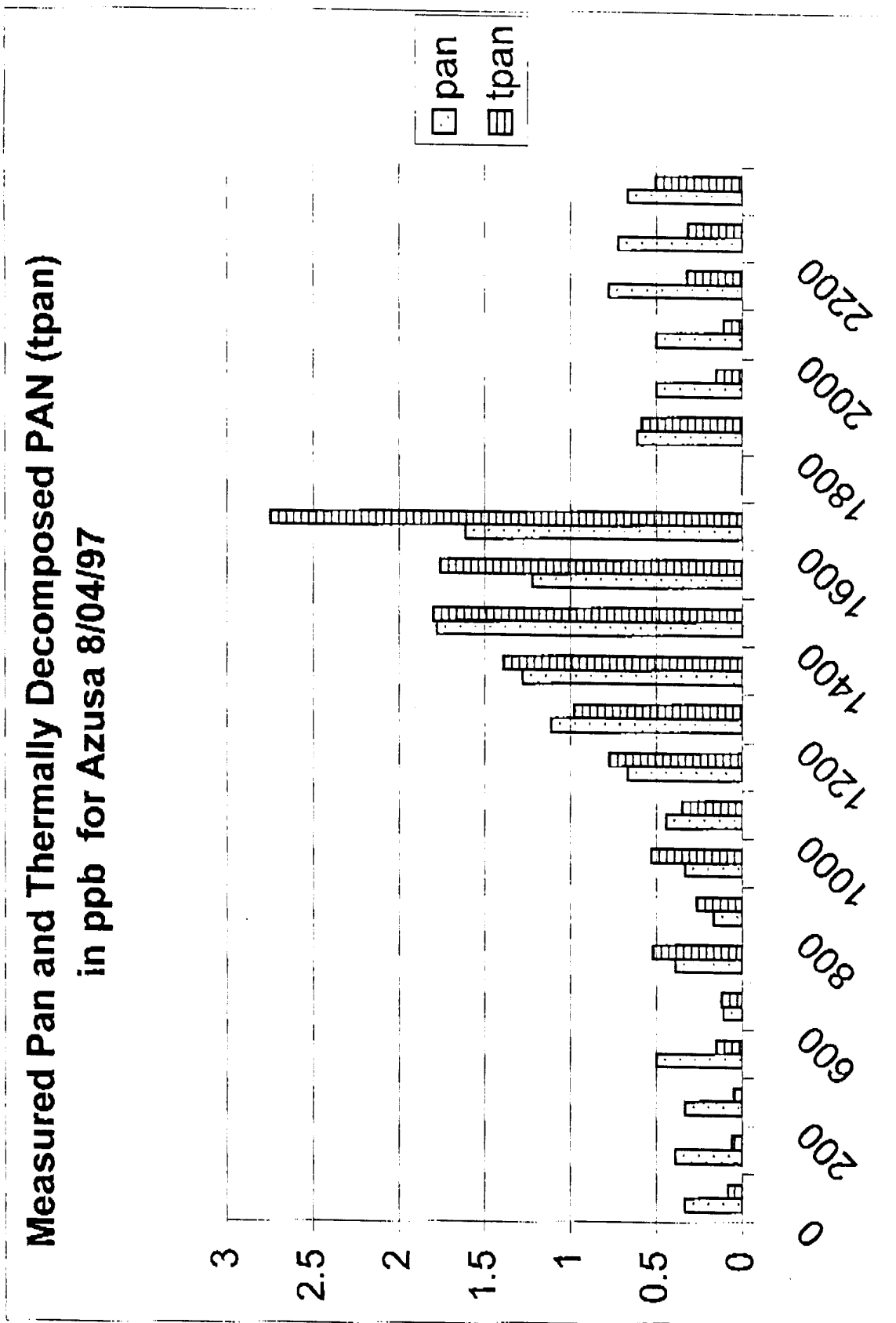


FIGURE 19(C)



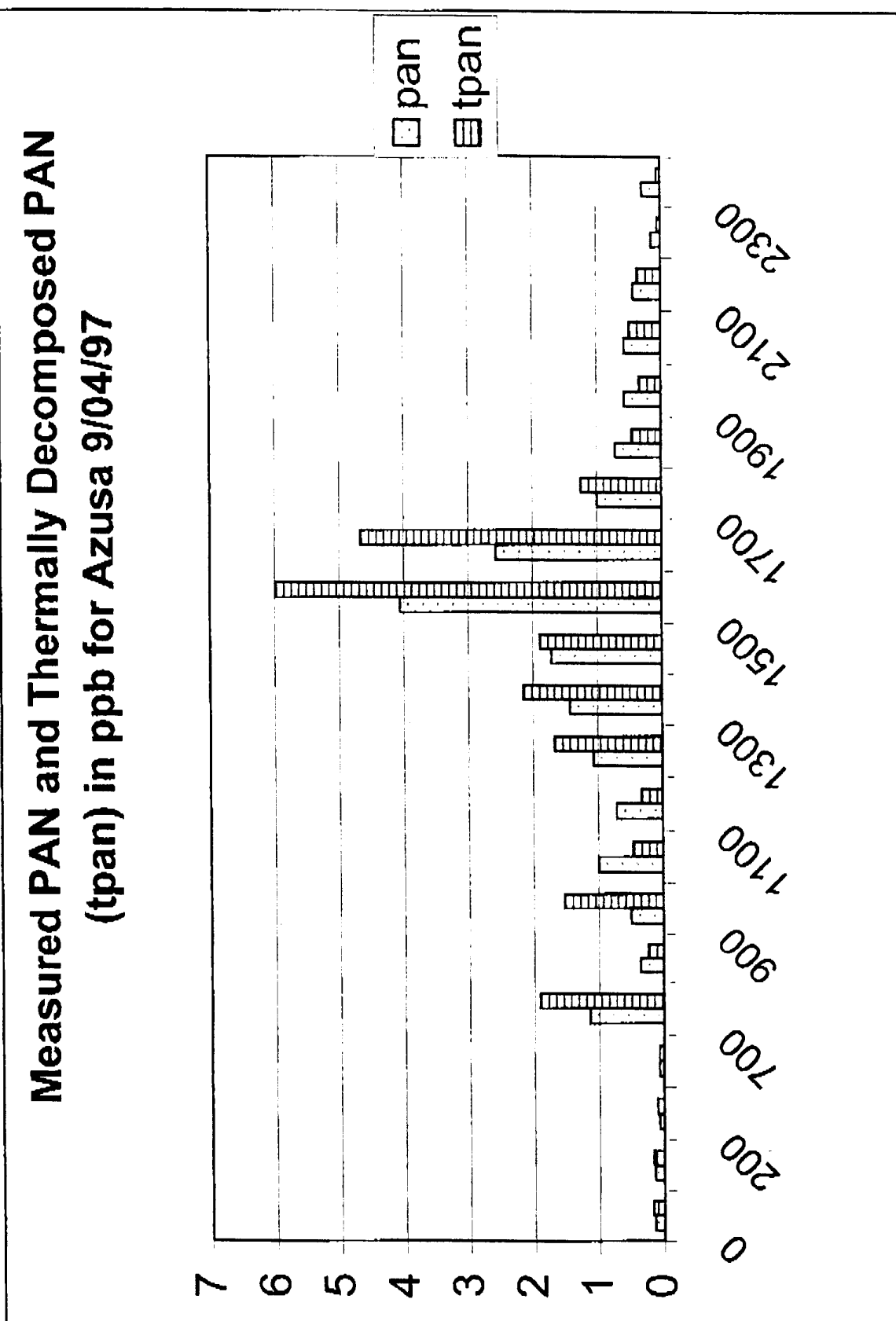


FIGURE 19(e)

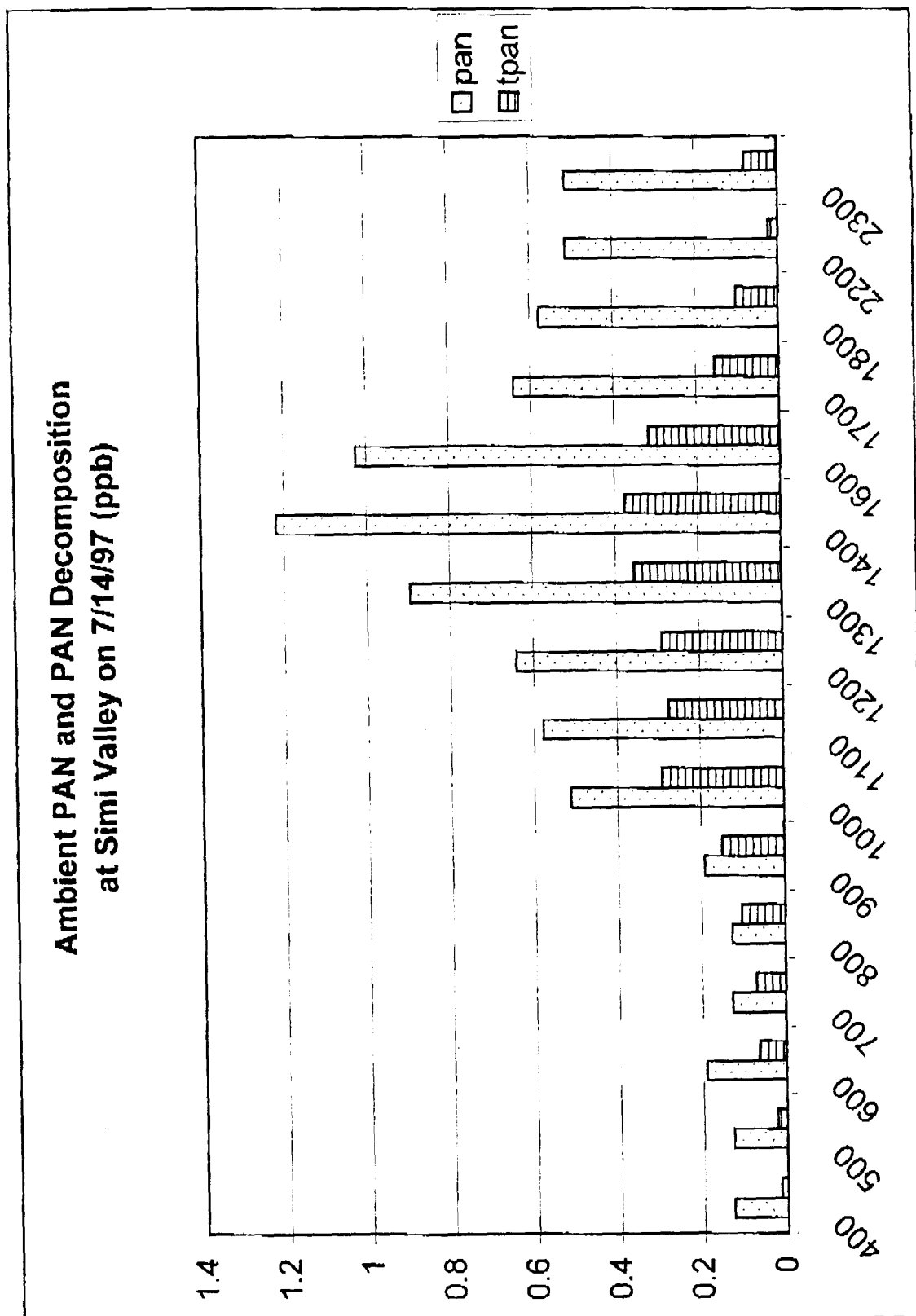
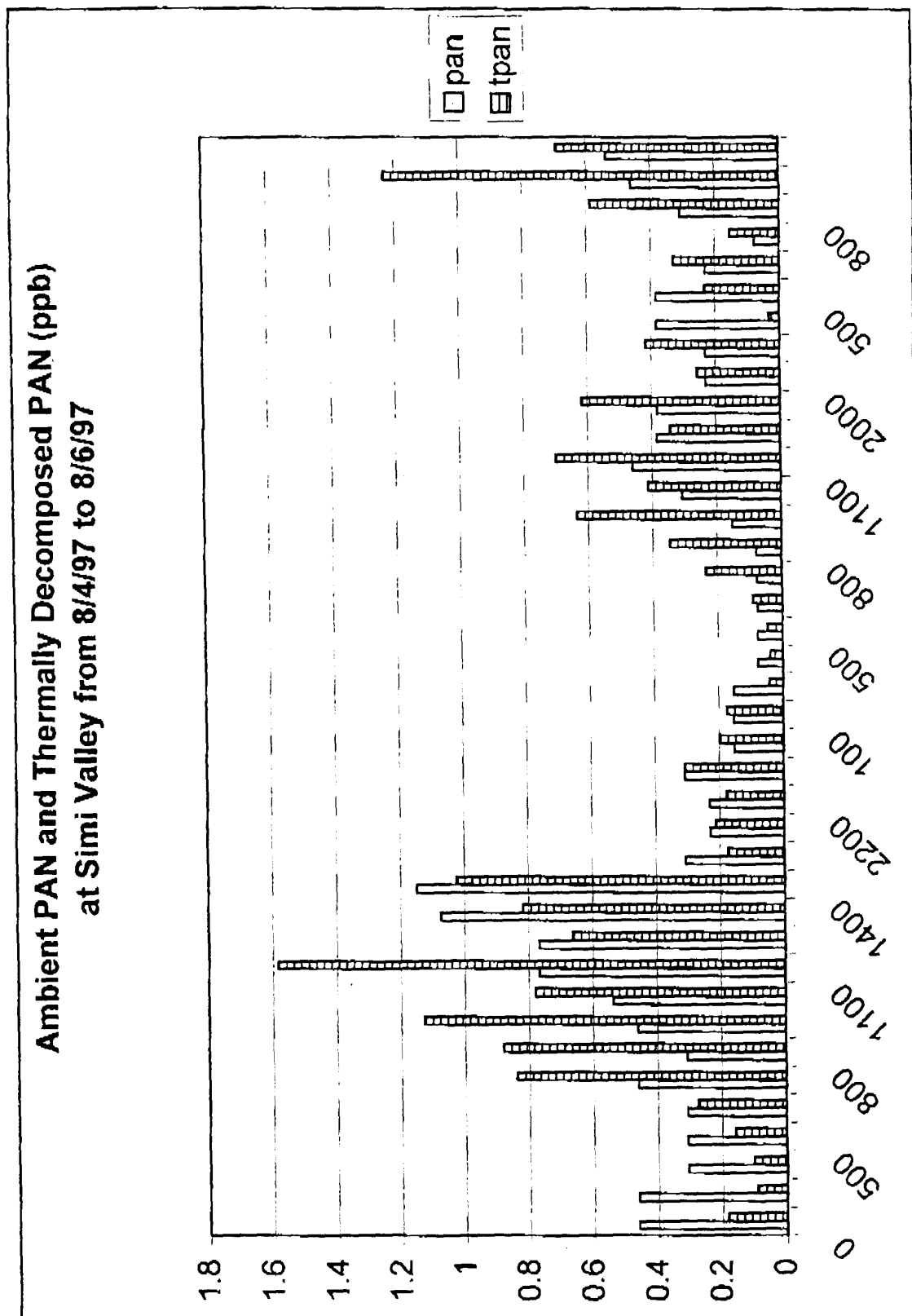
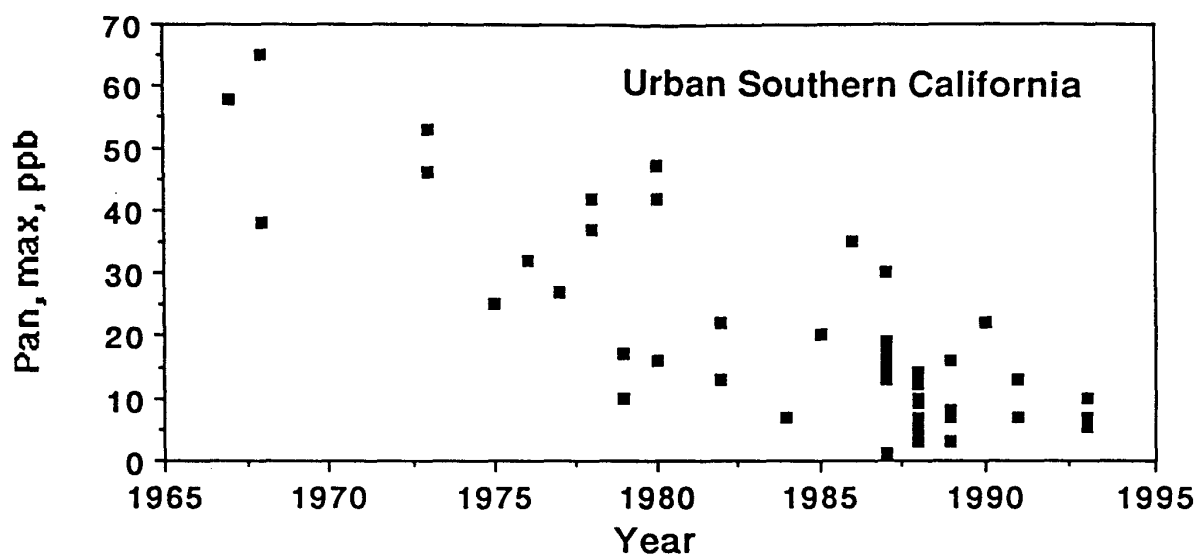


FIGURE 19 (f)



TO BE UPDATED



# FREQUENCY DISTRIBUTION OF PEROXYACETYL NITRATE (PAN), RIVERSIDE

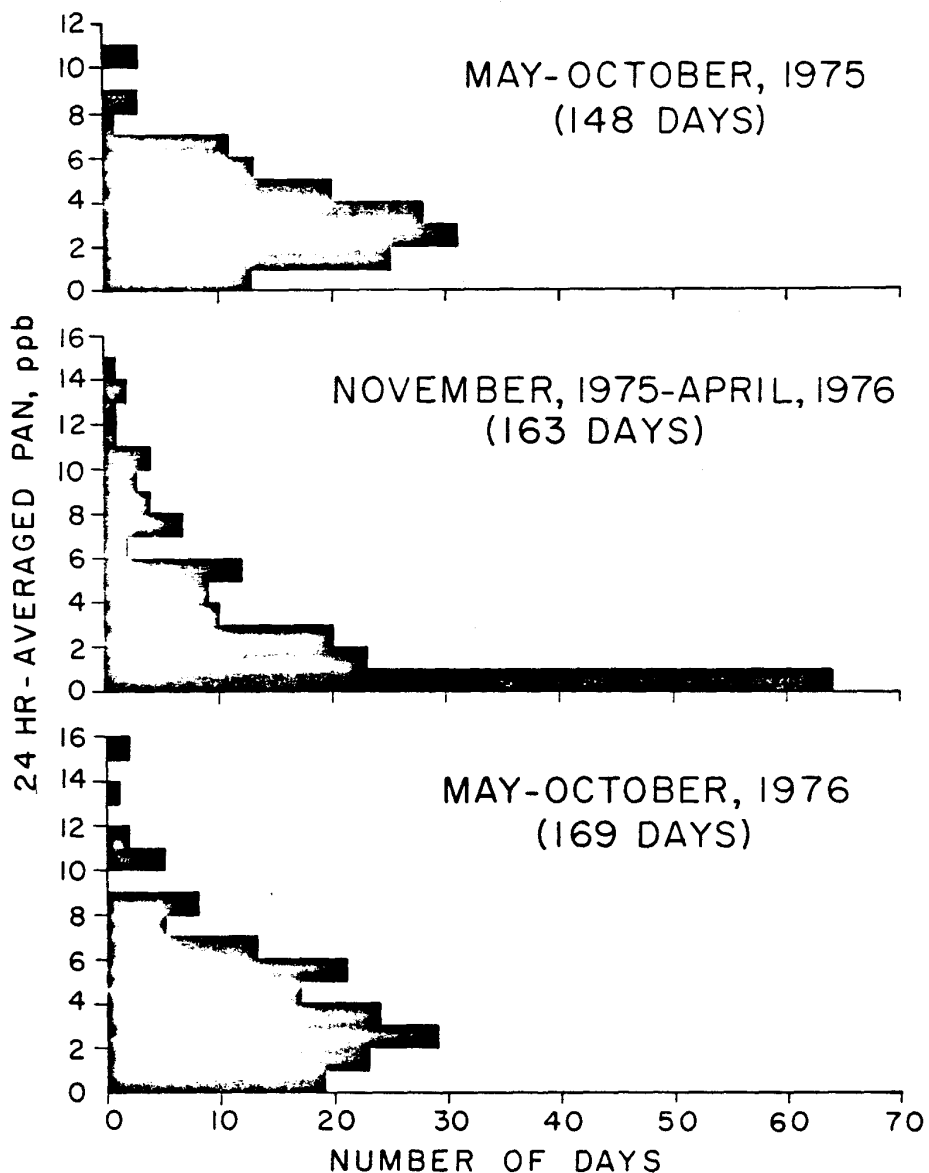
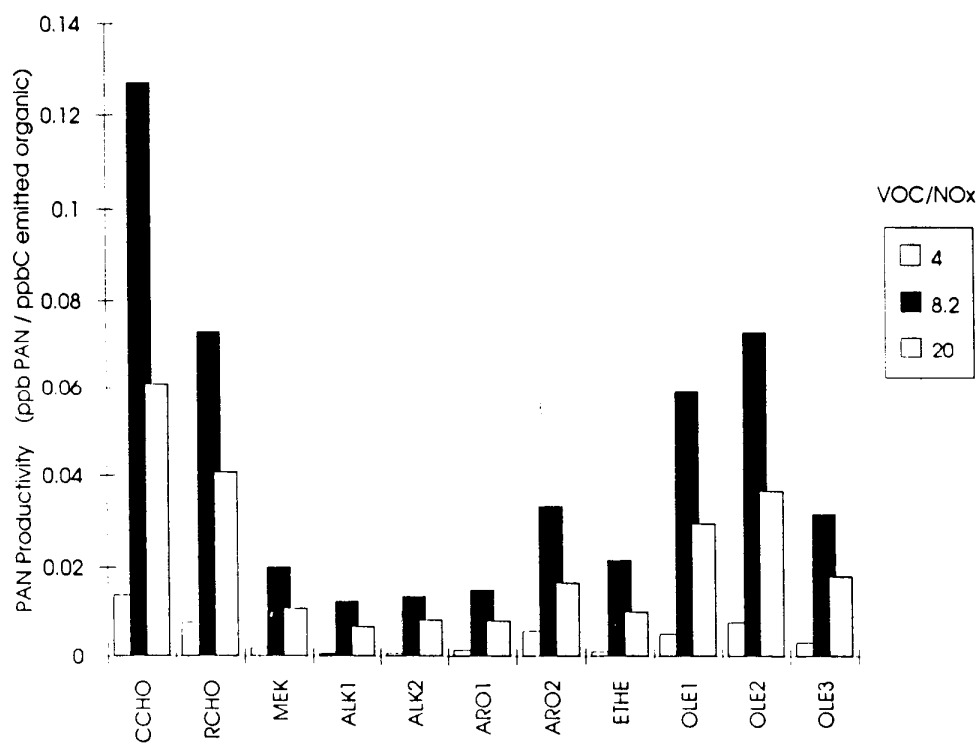
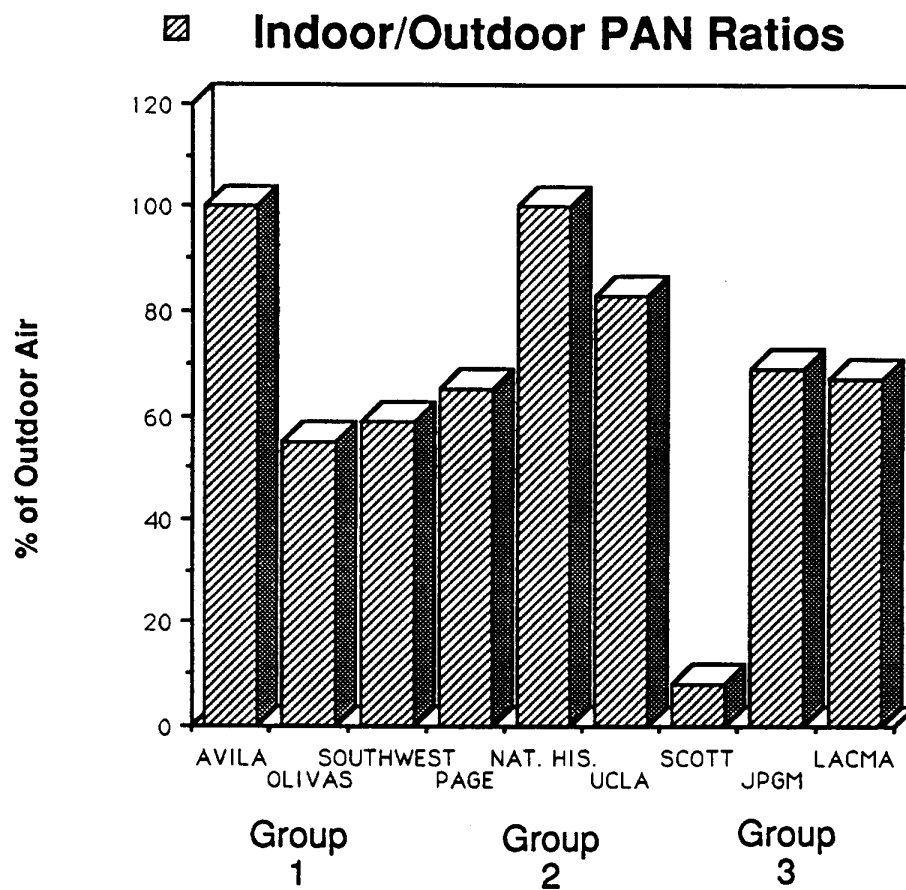


FIGURE 22

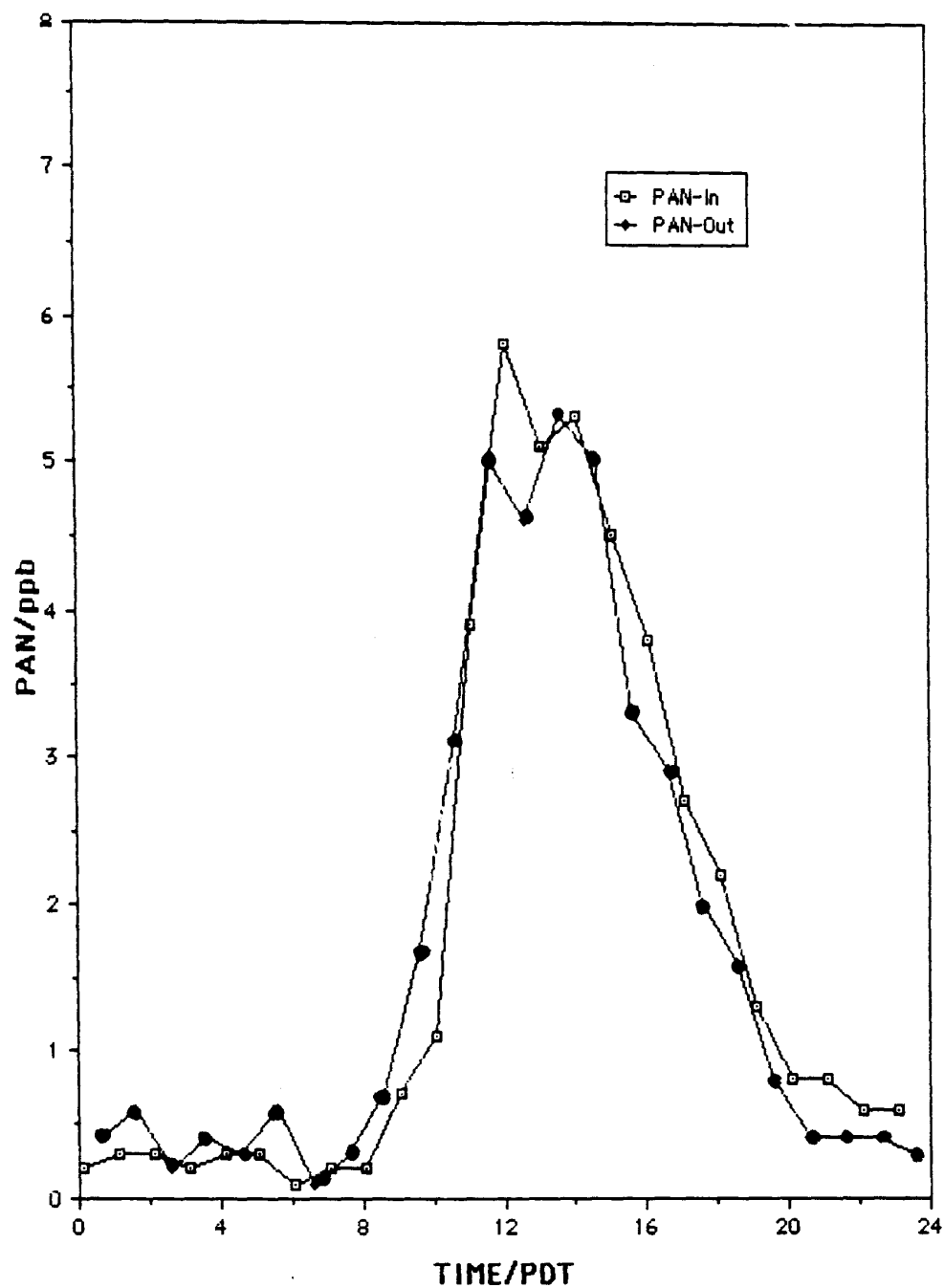




GROUP 1 : No Air Conditioning; High I/O Air Exchanges

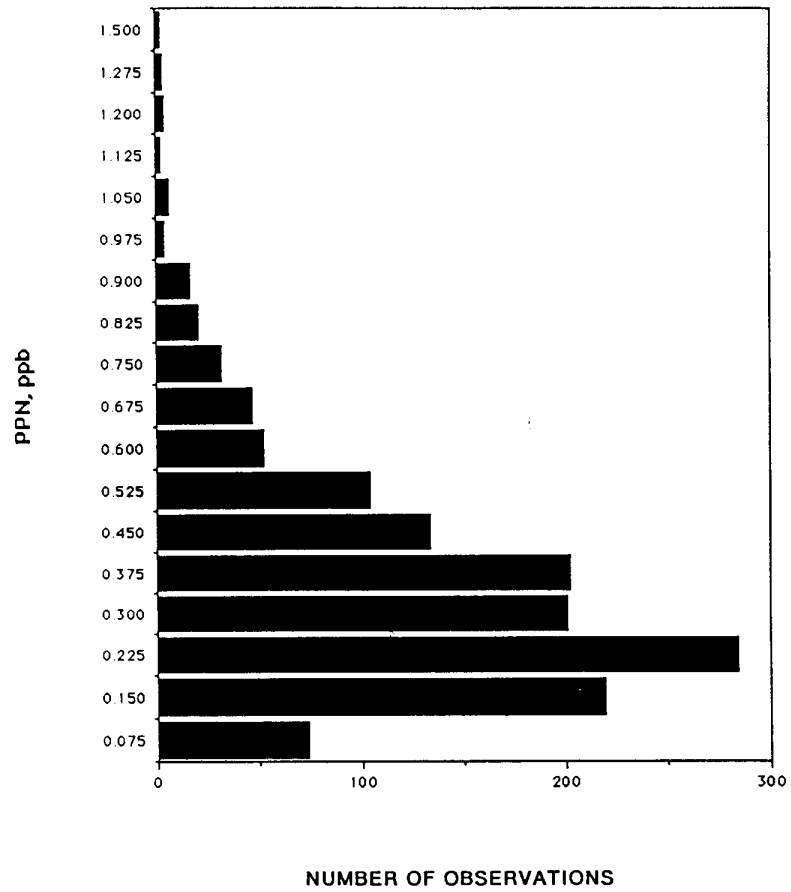
GROUP 2 : Air Conditioning; Intermediate I/O Air Exchanges

GROUP 3 : Air Conditioning; With Chemical Filtration



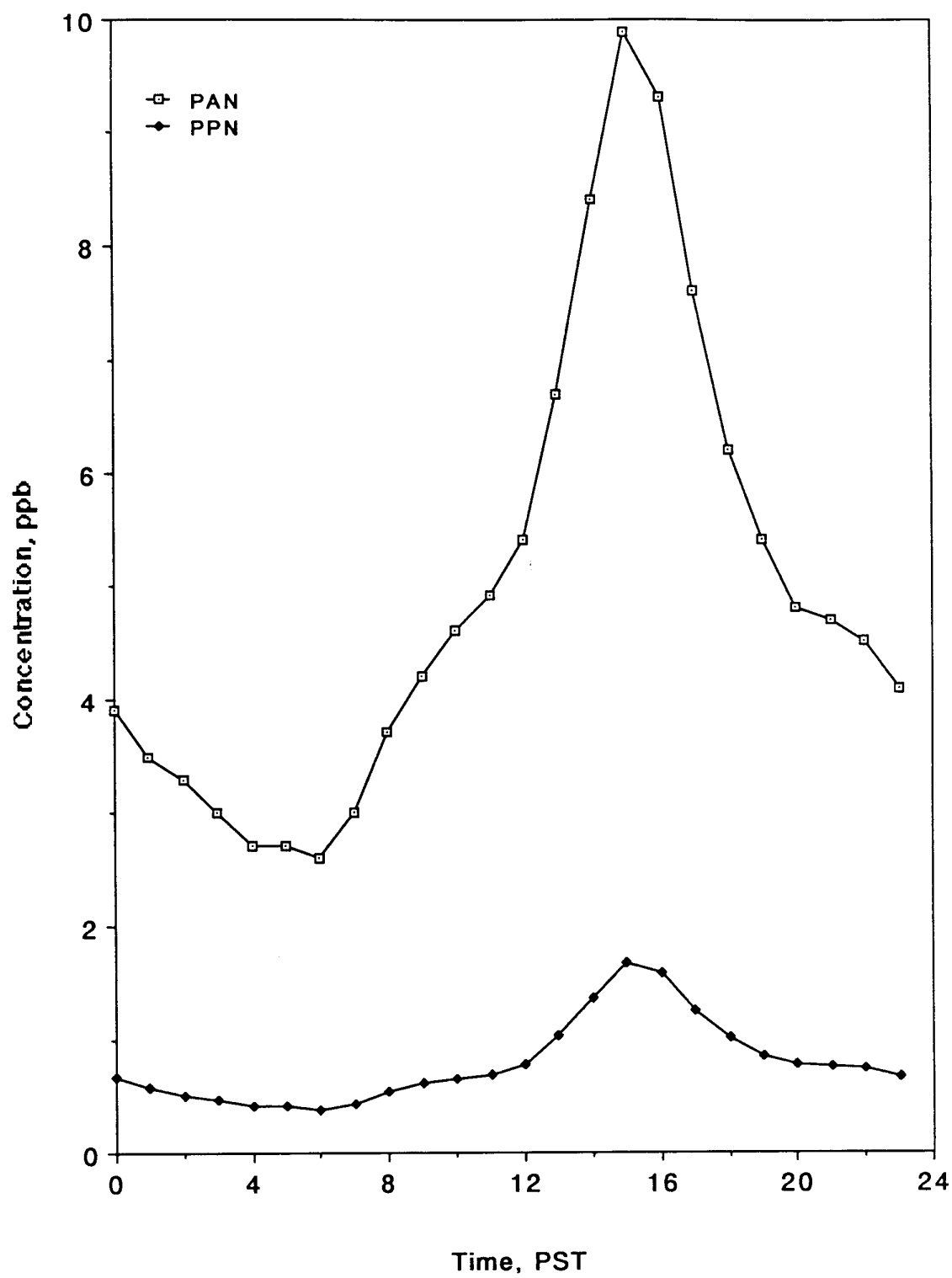
Composite (two weeks) diurnal profiles for indoor and outdoor PAN

FIGURE 25

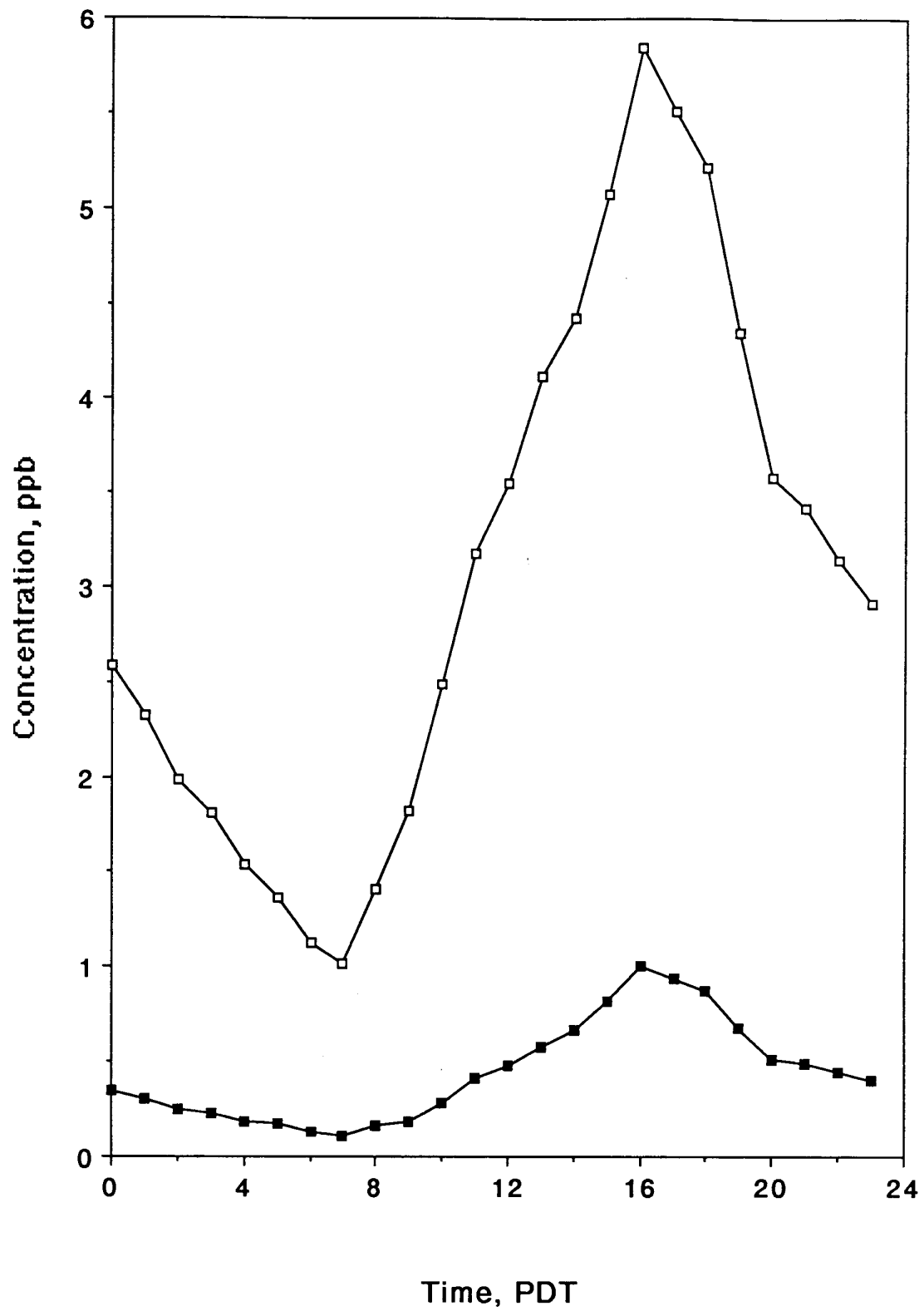




Average Diurnal Variation, Tanbark Flat 8/3 - 9/5/90



## Composite Data From Tanbark Flat August 1991



Composite Data From Franklin Canyon 9/4 - 9/12/91

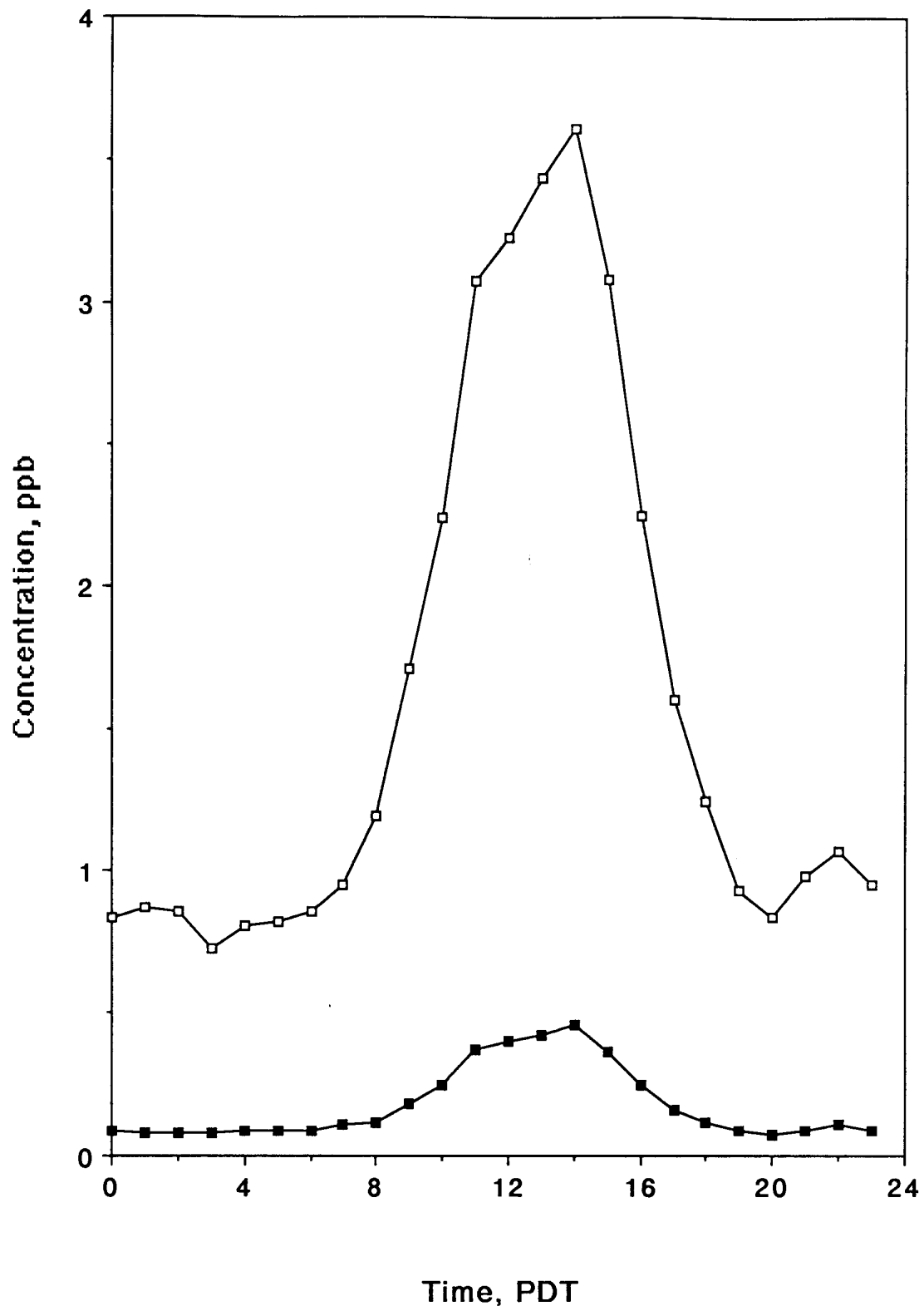
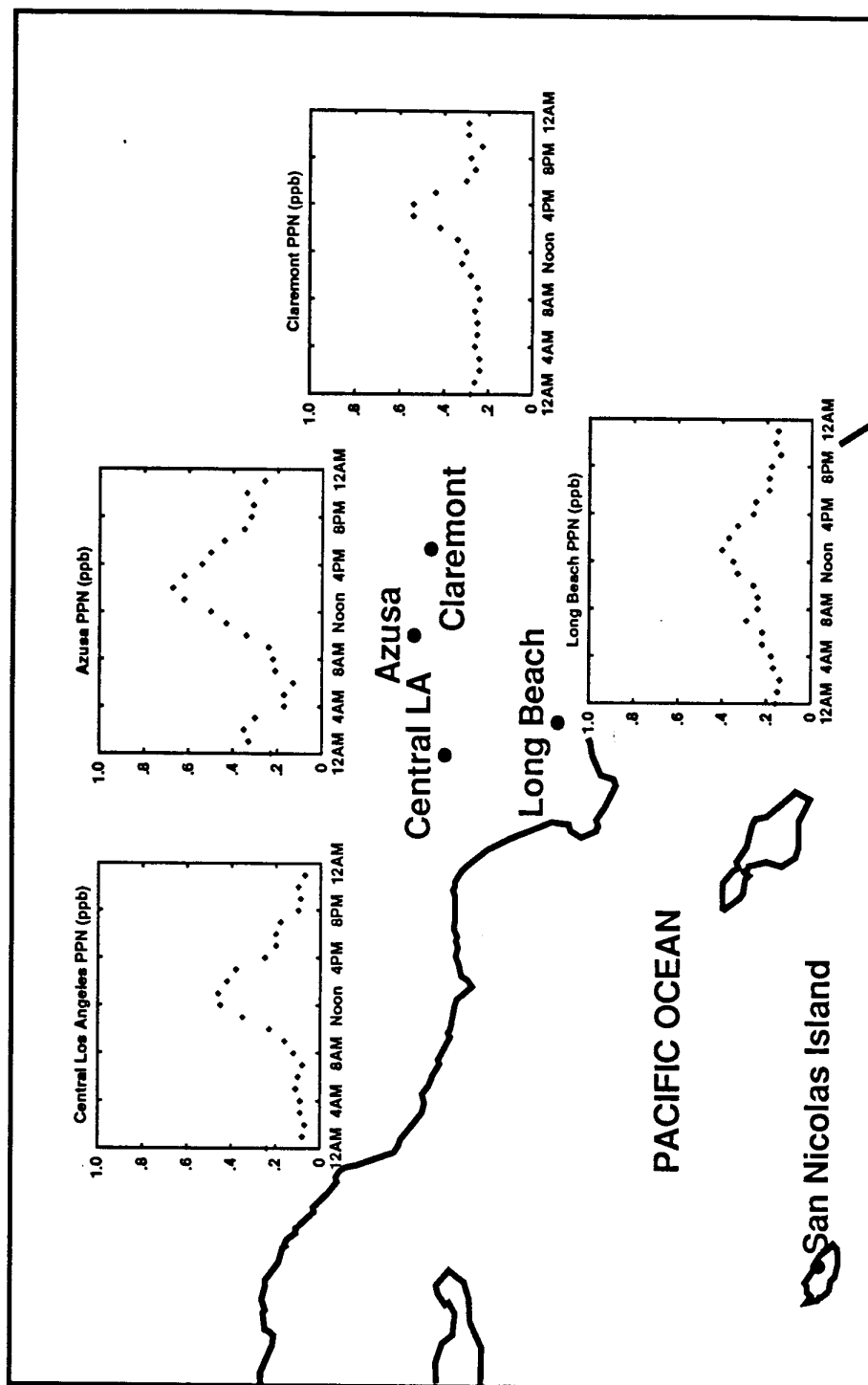


FIGURE 28



## DIURNAL VARIATIONS OF PPN / PAN CONCENTRATION RATIO

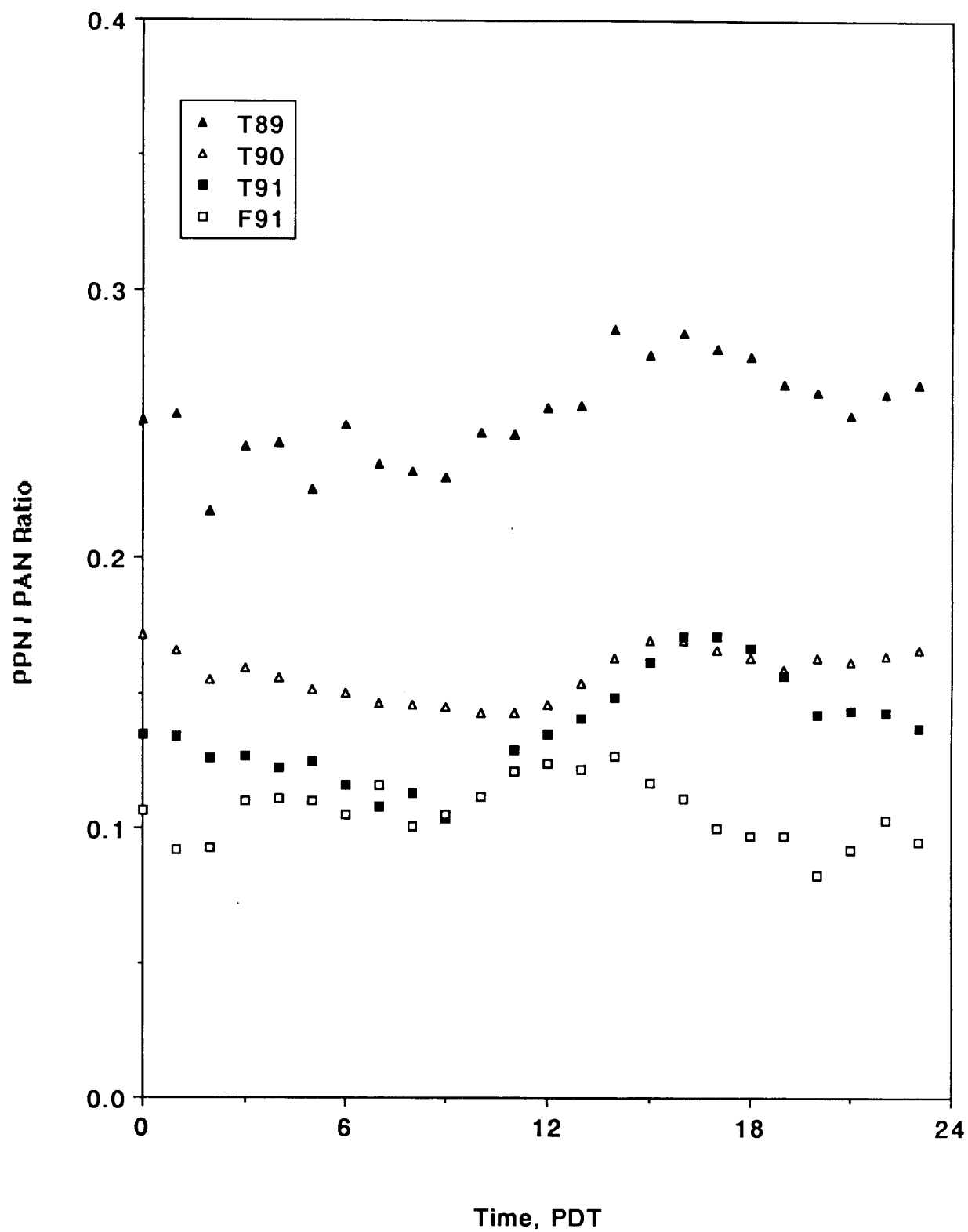


Figure 30

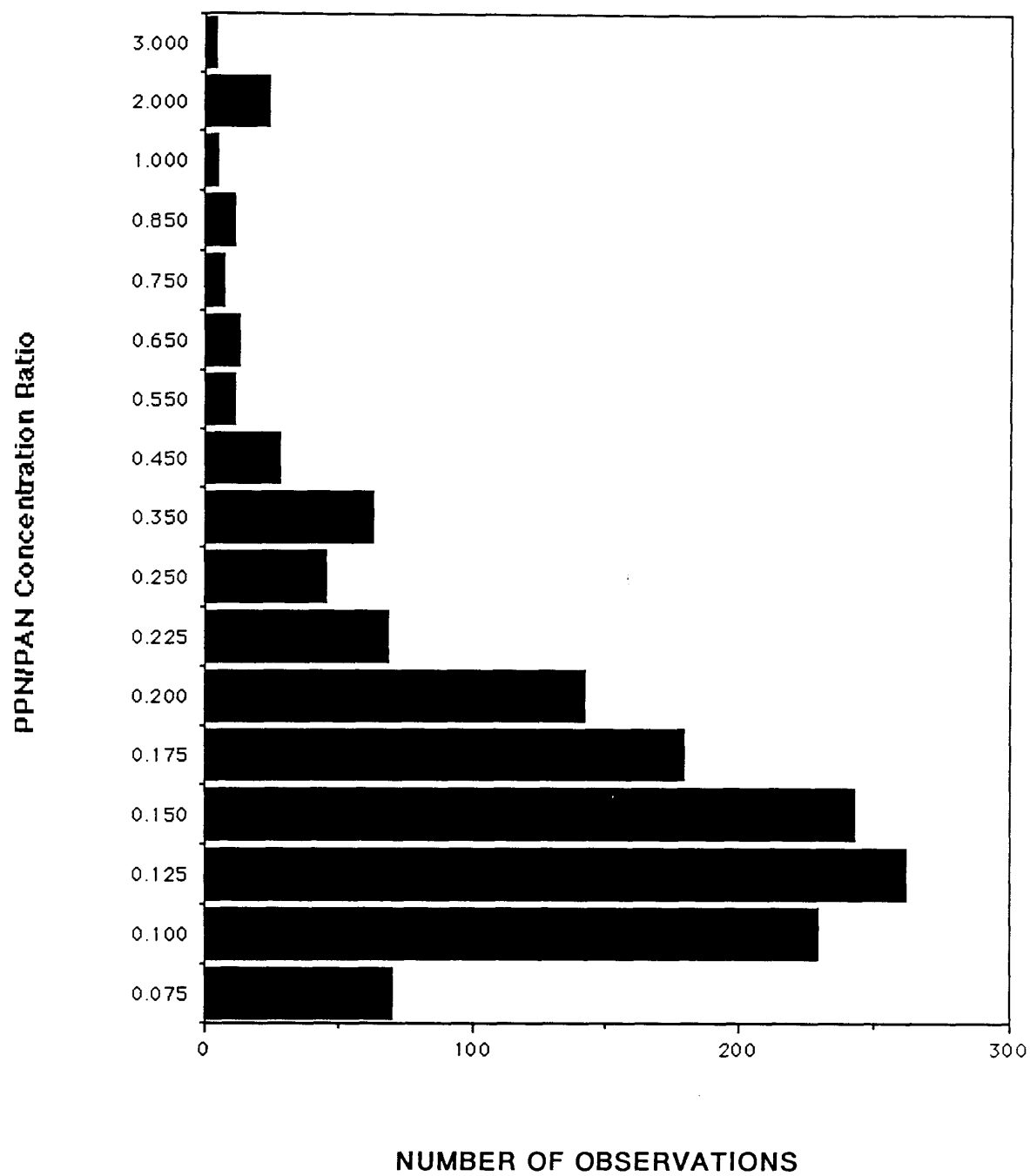
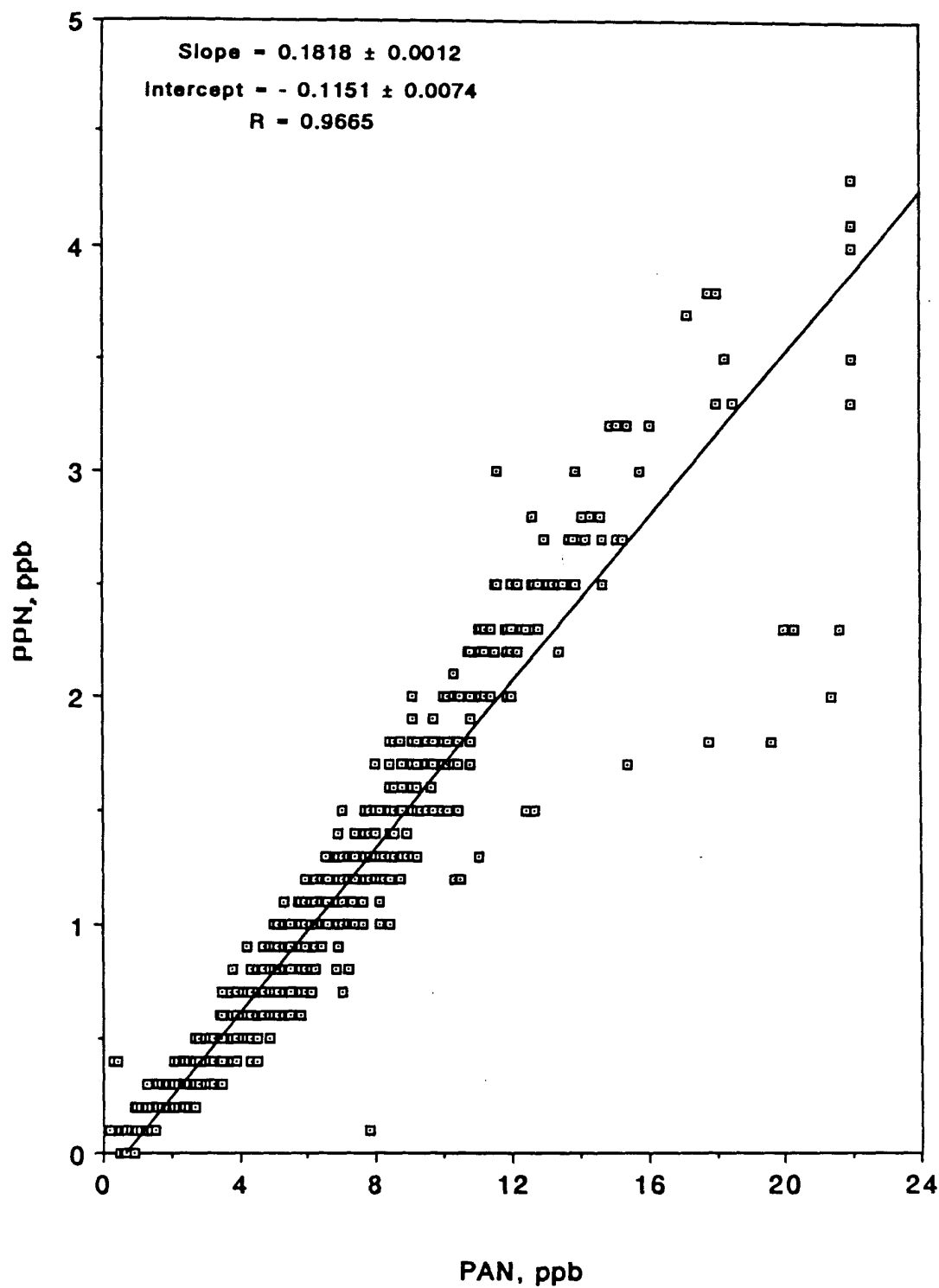


FIGURE 31(2)

PAN vs PPN, Tanbark Flat, 8/3 - 9/5/90



PAN vs PPN, Tanbark Flat, 8/5 - 8/26/91

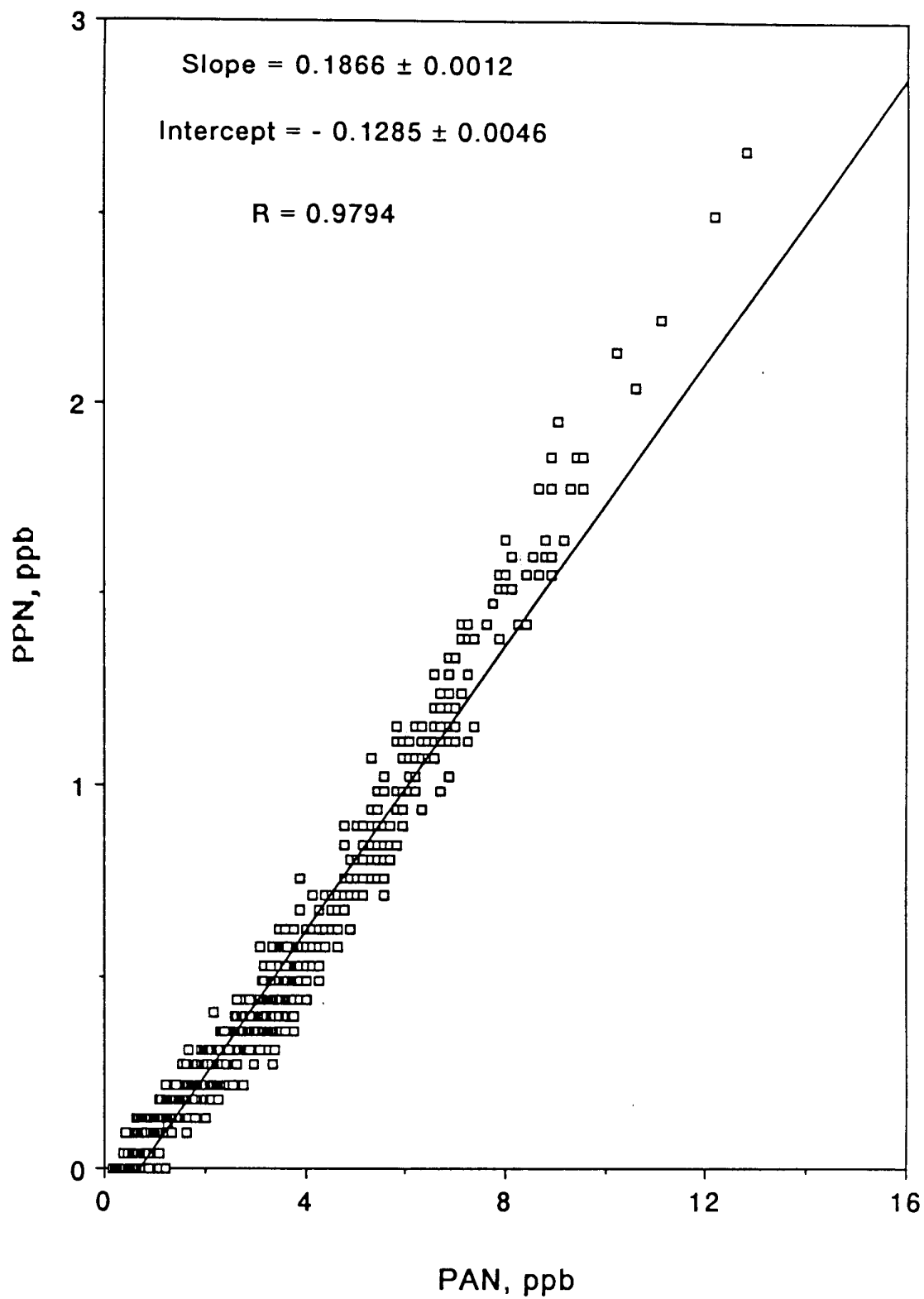


FIGURE  
31(c)

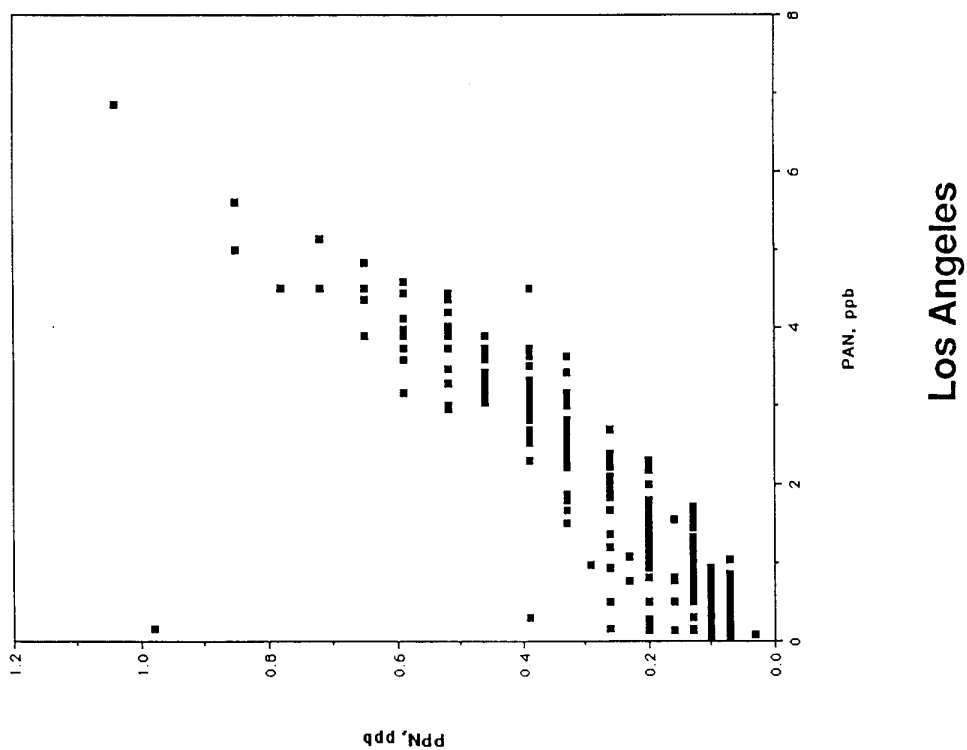
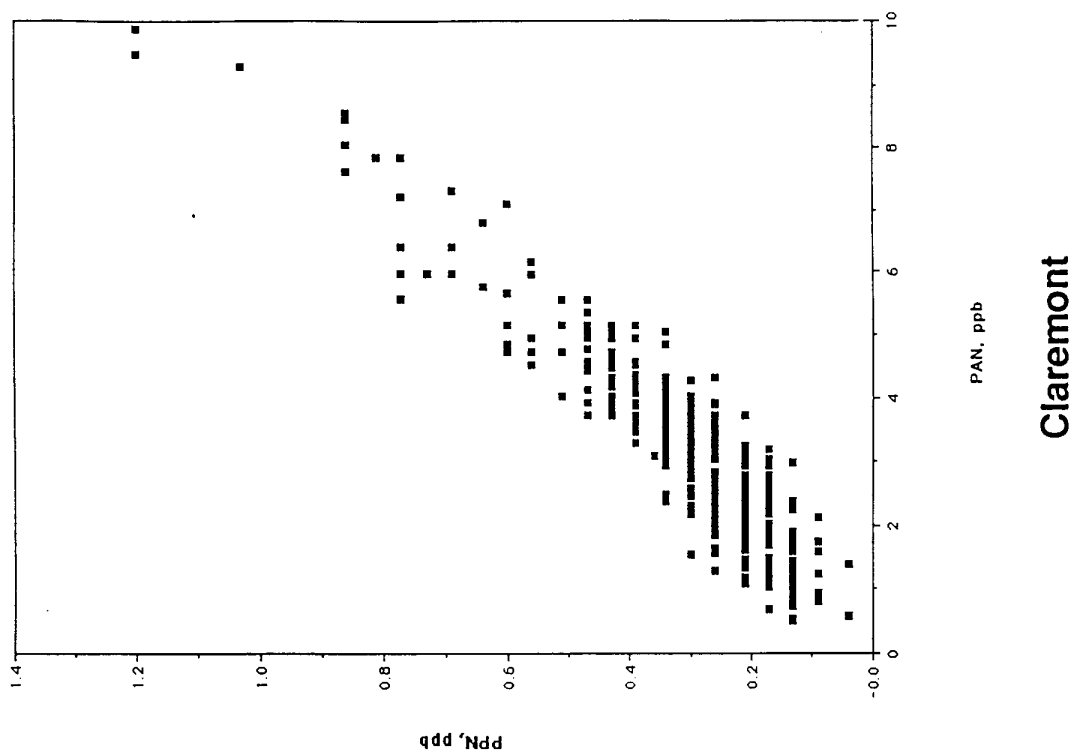


FIGURE 31(d)

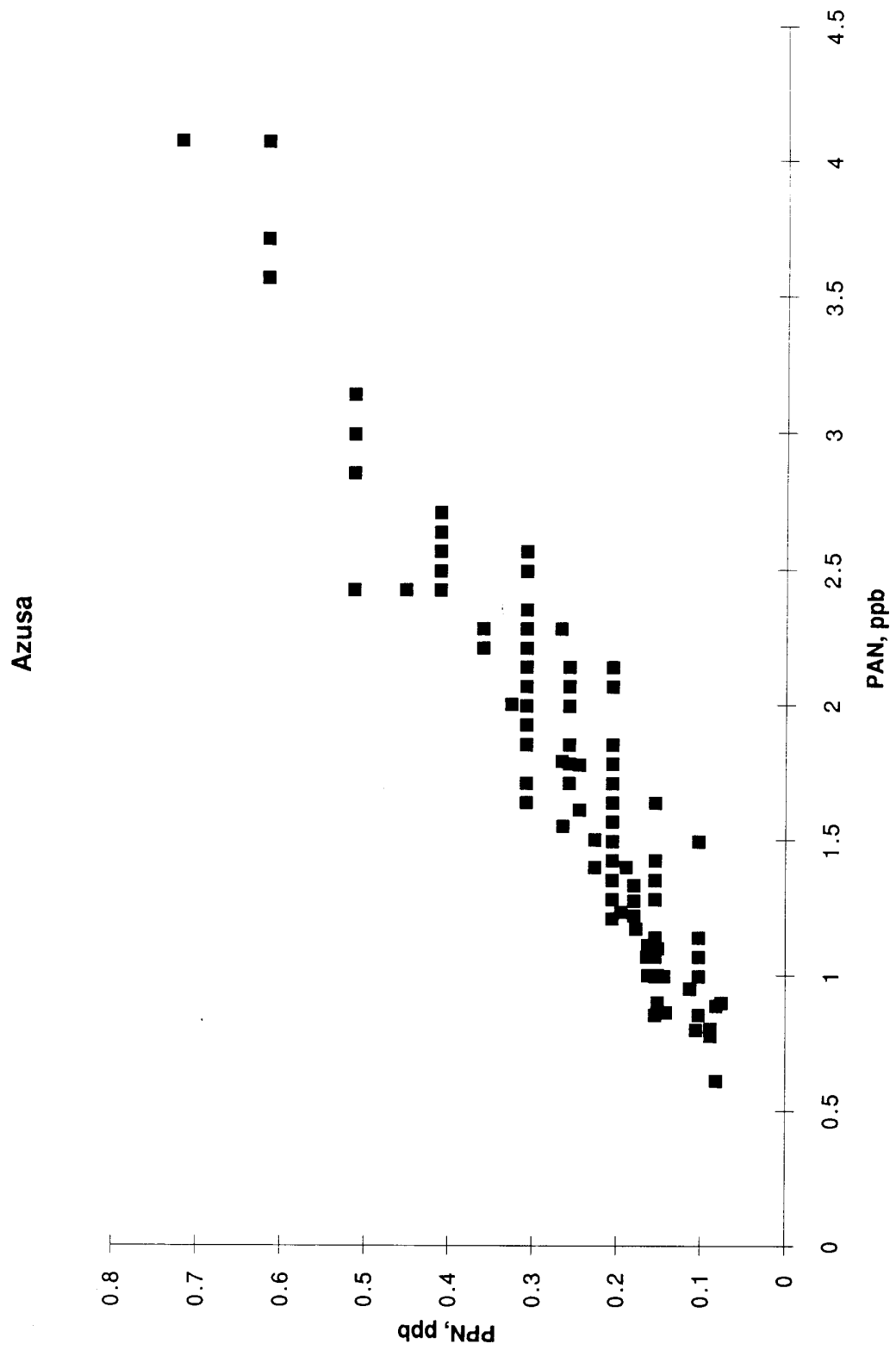


FIGURE 31(e)

